PRACTICAL
HYSICAL CHEMISTRY

BY

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WITH 124 FIGURES IN THE TEXT

SEVENTH EDITION, REVISED AND ENLARGED

BIBLIOGRAPHICAL NOTE

PREFACE TO THE SEVENTH EDITION

IN preparing the present edition, the opportunity has been taken not only of rewriting and of re-arranging considerable sections of the work, but also of making various additions which will, I hope, still further increase its usefulness. These additions include a thyratron relay and the use of refrigerator units for thermostats ; improved vapour density apparatus; maximum bubble pressure method of measuring the surface tension of liquids ; absorption spectra of coloured solutions ; use of the antimony electrode in determinations of hydrogen ion concentration and of the tungsten electrode in oxidation-reduction reactions ; boiling-point curves of binary mixtures of liquids and equilibrium curves in three-component systems. The number of experiments and of the applications of experimental methods previously described has also been increased.

I should like to take this opportunity also of thanking my many colleagues in different parts of the world for their kind criticisms and suggestions which have led to a progressive improvement of this book. I would earnestly beg these colleagues not to take it amiss if I have found myself unable to adopt all the suggestions which they have, out of their wide experience, so kindly made. The study of such subjects as ultra-violet and infra-red absorption spectra, magnetic susceptibilities, dielectric constants, unimolecular films, photochemical reactions, etc. are, of course, of the highest importance at the present time ; but I have been reluctantly compelled to omit discussion of them here. It has never been my aim to provide a comprehensive treatise on physico-chemical methods, and when I tried to write up these rather specialized subjects, I found that even a brief discussion, if it was really to be of use, would entail such

an increase in the size of the book that the consequent rise in price was bound to bear hardly on many students. I ask my colleagues to accept this as my excuse and would beg them still to give me the benefit of their criticisms and suggestions.

A. F.

UNIVERSITY OF ABERDEEN,
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PREFACE TO THE FIRST EDITION

DURING recent years it has come to be more widely recognized in our Universities and Colleges that the course of study for students of Chemistry, no matter to what special branch of the subject they may intend to devote themselves later, cannot be regarded as complete or satisfactory unless it include both systematic and practical Physical Chemistry. While, however, the student of practical Inorganic or Organic Chemistry has at his command an abundant supply of text-books, both elementary and advanced, the student of practical Physical Chemistry has hitherto been forced to rely, almost entirely, on the text-book of Ostwald or Ostwald and Luther. Although this forms in every way an admirable guide and book of reference for the advanced worker in Physical Chemistry, it has not proved itself suitable as a text-book for the general student of Chemistry, whose chief desire is to obtain some knowledge of the experimental foundations of the subject. It is, no doubt, to the lack of a suitable elementary text-book in which the student of Physical Chemistry can find sufficiently detailed guidance and direction in the carrying out of the more important physico-chemical measurements, that the complete or almost complete omission of practical Physical Chemistry from the ordinary course of chemical study in many of our British Universities and Colleges is largely due.

For several years practical Physical Chemistry has formed part of the regular laboratory course for students of Chemistry in the University of Birmingham ; and it is primarily for the benefit of these students that the present book has been written. It is hoped, however, that the volume may be of value for other students also, and may help to promote the more general introduction of Physical Chemistry into the courses of study in other Universities.

In making the choice of experiments described in the following pages, regard has been had to the requirements of the general student of Chemistry, and for this reason only typical methods and experiments, or such as are of funda-

mental importance in the study of Physical Chemistry, have been selected. The experiments are therefore designed, as supplementary to the more or less qualitative demonstrations in the lecture-room, not only to familiarize the student with the chief methods of experimentation and to assist him in understanding the general laws and principles of Physical Chemistry, but also to establish these more firmly in his memory.

With regard to the order of treatment of the different subjects, I have followed, for the most part, that adopted in my lecture course. But it is by no means necessary that the student should carry out the experiments in the order they are here described. The different chapters are, as far as possible, independent one of the other, and full freedom is therefore left to the teacher to take up the subjects in what order he may consider best.

Where the time that can be devoted to practical Physical Chemistry is limited, it may be found impossible for each student to perform all the experiments described in the following pages. In such cases it is very advantageous to group related experiments together, and to apportion the experiments among a group of students. Thus, for example, one student might determine the molar weight of camphor in benzene ; another, the apparent molar weight of benzoic acid in benzene ; while a third might determine the apparent molar weight of sodium chloride in water. In this way, each student would learn the method of molar weight determination by the freezing-point method ; and by comparing his results with those obtained by his fellow-students would obtain a very good idea of the principles involved in the different experiments carried out by them. This method of working enables each student to cover more ground than he otherwise would do, and is much more satisfactory than allowing two or more students to carry out one and the same experiment in common.

In conclusion, I would express my indebtedness to the text-book on Physical Chemical Measurements by Ostwald and Luther, to which all advanced students may be referred ; and I would also thank my colleague, Dr. A. du Pré Denning, not only for his assistance in reading the proof-sheets, but also for the friendly criticism which he was good enough to offer.   A. F.

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PRACTICAL
PHYSICAL CHEMISTRY

CHAPTER I

CALCULATION OF RESULTS AND ERRORS

SINCE it is only in rare cases that the numerical value of a physical property can be determined directly, it becomes necessary to *calculate* the value of the property from the different observations and measurements which have been made. Although this operation may necessitate the use of only simple arithmetical processes, both the method of calculation and the manner of expressing the result demand attention if one is to avoid useless labour and at the same time give correct and significant expression to the results of the measurements performed.

Number of Figures to be Employed.—Probably one of the first difficulties which confronts a beginner is to decide how many figures are to be employed ; for it is just as easy, and apparently more natural, to make the mistake of using too many as of using too few figures. Thus, in carrying out, say, the process of multiplication or division with two numbers, it appears to be very difficult for one to get rid of the idea that the greater the number of places to which the result is calculated, the more accurate must it be. However this may be with regard to the purely arithmetical value of the result, increase beyond a certain point in the number of figures intended to represent the value of an experimentally determined physical property is a useless waste of labour.

Since every measurement involves a certain error, or can be carried out only with a certain degree of accuracy, it is evident that the number expressing the value of a property depending on the measurement can only be approximate. However many figures one writes down, therefore, as the result

of a calculation, the accuracy of the value cannot be in-
creased beyond that determined by the errors of the measure-
ments. On the other hand, if too few figures are written
down, the statement of the result may be much less accurate
than the measurements allow. It is necessary, therefore, to
choose the number of figures so as to indicate the limit of
accuracy of which the measurements are capable. In order
to ensure this, the result should be expressed by such a
number of figures that all, except the last, are known with
certainty, and that, while the last figure is uncertain, the
error is not greater than ± 5 in the following place. This
constitutes the *maximum apparent error* of the number.

Thus, for example, in reading a burette, the error in read-
ing may be taken at about 0·01 ml. If, therefore, one wrote
down as the result of a reading, say, 22·4 instead of 22·40 ml.,
one would be committing the mistake of writing too few
figures ; for, according to the rule given, the number 22·4
would indicate that the true value lay between 22·35 and
22·45, and the apparent error is therefore five times greater
than the error of measurement. On the other hand, if, in
taking the mean of the readings 22·38, 22·40, 22·42, 22·39,
one wrote the result 22·397, one would commit the error of
writing too many figures, for this would indicate that the
error of measurement is only about $\pm 0·001$ ml. The number
should therefore be rounded off to 22·40. For the purposes
of further calculation, however, one figure more is used, *i.e.*
one would use 22·397.

Calculations with Approximate Numbers.—Having decided
the number of figures to be used in expressing the result of
a given measurement, the question still remains as to how
many figures are to be retained in a final result obtained
with these approximate numbers by the processes of addi-
tion, subtraction, multiplication or division.

In the case of *addition* and *subtraction* of approximate
numbers, the greatest apparent error in any of the numbers
gives the maximum apparent error in the final result. Thus,
if the different numbers have all the same apparent error, the
result will also have this apparent error.

For example, in the addition—

the maximum apparent error in each of the numbers is $\pm$0·05 ; and this is also the maximum apparent error in the result, because the errors in the two numbers of the sum may have the same or opposite signs with equal probability, and may therefore with equal probability increase or cancel each other.

In the case, however, of the addition—

$$\begin{array}{r} 22\cdot4 \\ 120\cdot106 \\ 12\cdot2245 \\ \hline 154\cdot7305 \end{array}$$

the maximum apparent error in the result must be $\pm$0·05, which is the greatest apparent error in any of the single numbers (22·4).   Consequently there is a derived error of 5 units in the figure 3, and the result ought therefore to be written 154·7 ;   although if the number is to be used in further calculations it is better to retain, as is usual, one figure more, *i.e.* to use 154·73.

Not only should one not write all the figures 154·7305 as the final result, but one should seek to acquire the habit of not writing down the unnecessary figures in the numbers to be added.   Thus, instead of writing 120·106 one should write 120·11 ;   and instead of 12·2245 one should write 12·22.   In these cases the second figure of the decimal is retained in order to avoid introduction of fresh errors in rounding off the number.

With regard to this operation of *rounding off* a certain number, the rule is that if the number in the place following the last to be retained is equal to or greater than 5, one unit should be added to the last place retained.   Thus, if it is wished to retain only the second place of decimals, one should make 12·224 into 12·22, 12·225 into 12·23.

In the case of *multiplication* and *division* of numbers, one is concerned only with the *relative errors* or *proportional errors* in the numbers, not with the apparent or the absolute errors ;   and it has to be remembered that a given relative error in the numbers will produce a corresponding relative error in the result.   Thus, in determining the area of a rectangle, if it is found by measurement that the sides are equal to 100·0 and 10·0 cm. respectively, there is a possibility of error in measurement in both cases.   If both

lengths have been measured with the same absolute error, say, 0·1 cm., then the relative errors in the two measurements will be 0·1 and 1·0 per cent. respectively. But if the correct lengths were 100·0 and 10·1 cm. respectively, the area would be not 1000 sq. cm., but 1010 sq. cm., or 1 per cent. greater. If the lengths were 100·0 and 9·9 cm. respectively, the area would be 990 sq. cm., which again differs from the number 1000 by one-hundredth of the total value, *i.e.* by 1 per cent.

It will, of course, be quite evident that the error in the final area caused by the possible error in the length of 100·0 cm. can amount to only 0·1 per cent. ; that is, it is negligible as compared with the much greater error produced by the uncertainty of the number 10·0. Whenever, therefore, in an operation involving the multiplication of factors, the relative error in one is much greater, say from five to ten times greater than the relative errors in the other factors, the latter errors may be neglected altogether, and the error in the result will be determined only by the greatest relative error in the factors.

Suppose, therefore, that one has to multiply 2·3416 by 2·55, and suppose each of these numbers to have the maximum apparent error ; then the relative error in the first number is about 5 in 230,000, and the error in the second number is about 5 in 2600. Evidently, therefore, the result of the multiplication will also have an error of about 5 in 2600, or 0·2 per cent. Consequently it would be quite incorrect to perform the multiplication in the ordinary manner, and write the result as 5·971080 ; for this result has a derived error of 0·2 per cent., or of about 1 unit in the second place of decimals. All the figures after this are therefore meaningless, and should be discarded, the result being written 5·97.

What has been said with regard to multiplication holds equally for division ; for in this case also, the greatest relative error in divisor or dividend, if it be five or ten times greater than the other relative errors, will determine the relative error in the result.

EXAMPLE—

$$\frac{1·45 \times 5·680}{10·234} = 0·80477.$$

Since 1·45 contains the greatest relative error, viz. 5 in 1500, or about 0·3 per cent., the final result will have an equal relative error

from this cause. Hence there will be an error of about 2 units in the third place of decimals, or, in other words, the 4 is somewhat uncertain. One may therefore write the result 0·805 ; and for further calculations one may use 0·8048.

Methods of Calculation.—From what has just been said, it will be seen that calculations carried out in the ordinary way frequently involve the manipulation of a number of useless figures, and that several of the figures obtained as the result of laborious calculation are afterwards discarded altogether as meaningless.

Much useless expenditure of energy may be avoided by adopting abbreviated methods of multiplication and division, and by the use of logarithms and of the slide rule.

Logarithms.—In making calculations with the aid of logarithms, the precautions adopted in the preceding methods for the avoidance of unnecessary figures are introduced automatically, if it be so arranged that the number of figures in the logarithm is greater by one than the number of figures in the least accurate of the numbers involved in the calculation. In this way one ensures that the error in the result shall not be greater than the error in the numbers from which the result is obtained. If one had to multiply $2·54 \times 4·3664 \times 0·89676$, one should use 4-place logarithm tables, and the second and third numbers should be rounded off to 4·366 and 0·8968.

The error inherent in the logarithm itself decreases with the number of places in the logarithm, each additional figure in the logarithm being accompanied by about a tenfold decrease in the error. In the case of 4-place logarithms, the maximum possible error introduced into a calculation through their use may be taken as about 1 in 3000. For work of moderate accuracy, 4-place logarithms will be sufficient ; but in some cases, the error so introduced is greater than that due to experiment, *e.g.* determinations of density. In the latter cases, therefore, where the accuracy of the calculation is desired to be equal to the accuracy of the experiment, logarithms with 5 or 6, and even, in more exceptional cases, 7 places should be used.

The Slide Rule.—In many of the cases mentioned in the preceding pages, one was dealing with calculations in which the error involved was much less than that usually found in any but the best experimental work ; and in few or none of the experiments described in the following pages will an

accuracy in calculation be called for greater than can be obtained by the use of 4-place, or, at most, 5-place logarithms. Frequently, the accuracy required will be considerably less.

For all calculations where the required accuracy of experiment or calculation is not greater than about 1 in 500, the slide rule is of great assistance. With this instrument various degrees of accuracy can be obtained according to the size of the rule, but with the ordinary size of slide rule (25 cm. in length) the accuracy obtainable may be put down at about 1 in 500 to 1 in 800.

Errors.—The determination of the value of a physical property is always liable to errors of various kinds, so that in all cases the result of an observation or measurement is only an approximation to the truth. The two chief kinds of errors are : *constant errors* due to some error in the apparatus, or to the neglect of certain factors which exercise an appreciable effect, and *accidental errors* or *errors of observation*.

In the case of constant errors, the different values of the given magnitude may differ by a very small amount from one another, but may nevertheless differ by a comparatively large amount (the deviations being all in the same direction), from the true value. It is evident, therefore, that increasing the number of determinations will not in that case increase the accuracy of the result ; and to exclude the constant errors, it is necessary to vary the method of observation or to alter the conditions of experiment. This also includes calibration of apparatus, purification of materials, etc.

In the case of errors of observation, the results of the different determinations may vary in either direction from the truth, *i.e.* the errors may have a positive or negative effect. Thus, in volumetric analysis the burette readings may fluctuate, so that one obtains such numbers as 20·22, 20·26, 20·24, 20·22, 20·23. It is necessary, therefore, to decide which of these numbers, lying within the limits 20·22 and 20·26, is nearest to the truth. In all such cases, when one is dealing with a series of measurements of the same property, carried out with the same care, the best representative number is the *arithmetical mean* of the different numbers.

In certain other circumstances, individual errors of observation, can be diminished by a graphic method. Thus, in studying the variation of a magnitude with change of condition, *e.g.* change of viscosity with temperature, or the

alteration of the freezing-point of a solution with composition, the best values of the magnitude are obtained by plotting the results, say in rectangular co-ordinates, and drawing a " smooth curve " so as to take in as many of the individual observations as possible.

In this way one can obtain not only the best values of the magnitude under the particular conditions of the experiments, but also under other conditions, by taking the different points on the curves (*Interpolation*).   It must, however, be remembered that the numbers near the ends of the curve are liable to greater errors than near the middle, because the position of the curve near its ends becomes doubtful.

Influence of Errors of Observation on the Final Result.— It has already been stated that the value of a magnitude is obtained only by indirect measurement ; by the determination, that is to say, of another magnitude to which the first is related in some definite manner.   Thus, if it is desired to determine the length of the circumference of a circle use can be made of the relationship, circumference $=2\pi r$; and by determining the value of r one can then calculate the value of the circumference.   The circumference is therefore given as a product, and as the numbers 2 and π are free from error, it follows from what has previously been said, that the relative error in the final result will be the same as the relative error in r.   If r can be measured with an error of only 0·1 per cent., then the error in the value of the circumference need not be greater than 0·1 per cent.   It is necessary, therefore, that the value taken for π should be correct to less than 0·1 per cent.

On the other hand, suppose that one wishes to determine the area of a circle by means of the relationship, area $=\pi r^2$, then an error of 0·1 per cent. in the determination of r will cause an error of 0·2 per cent., or twice as great an error, in the result.

Whenever, therefore, the value of a magnitude is proportional, directly or indirectly, to the quantity measured, the relative error in the result will be, numerically, the same as the relative error in the quantity measured.

Thus, if $x \propto y$, an error of $\pm a$ per cent. in y will cause an error of $\pm a$ per cent. in x ; or if $x \propto \dfrac{1}{y}$, an error of $\pm a$ per cent. in y will cause an error of $\pm a$ per cent. in x.

When, however, the value of a magnitude is proportional to the nth power of the quantity measured, the relative error in the latter will be magnified n times in the result.[1]

In the above cases, it has been assumed that the value of a magnitude depends only on the measurement of one quantity. In most cases, however, a result is obtained by combining different kinds of measurements, and the accuracy (*i.e.* the relative error) of the final result will depend on the accuracy of the several determinations. Thus, the determination of the molecular weight by the cryoscopic method involves measurements of weight and of temperature ; the determination of the velocity of a reaction involves quantity and time. Now, it will be readily understood that some of these quantities are capable of more accurate measurement than others, but there would be no advantage in determining some of the factors with very great accuracy, if the errors involved in any of the other factors are much greater. This should always be borne in mind, as there is always a tendency to think that the accuracy of the final result can be increased by carrying out every measurement with the maximum degree of accuracy of which it is capable. Remember that the accuracy of the final result is influenced chiefly by the accuracy of the *least accurate* measurement ; and if the errors in the other factors are considerably less, say five or ten times less, then they may be neglected altogether.

In carrying out any composite determination, or one involving several different kinds of measurement, one should, before proceeding to carry out the actual determinations, first ascertain what is the influence on the result of a given error in each of the individual measurements, so that, on the one hand, special attention may be paid to those measurements having the greatest influence on the result, and, on the other hand, unnecessary excess of accuracy may be avoided in the case of the other measurements.

To do this, write down the expression giving the relation between the final result and the different measurements from

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[1] These conclusions can be readily reached by differentiation. Thus, if $x = k \cdot y$, $dx = k \, dy$, or $\dfrac{dx}{x} = \dfrac{k \, dy}{ky} = \dfrac{dy}{y}$. That is, the relative error $\left(\dfrac{dx}{x}\right)$ in x is equal to the relative error $\left(\dfrac{dy}{y}\right)$ in y.

Again, if $x = k \cdot y^2$, $dx = k \cdot 2y \, dy$; and $\dfrac{dx}{x} = \dfrac{2k \cdot y \, dy}{k \cdot y^2} = \dfrac{2 \, dy}{y}$. That is, the relative error in x is twice as great as the relative error in y.

which it is obtained, and then, taking each factor in turn and regarding all the others as being constant, determine its influence on the final result as described above. Thus, for the determination of the molecular weight by the cryoscopic method, one has (p. 125) $M = K \cdot \dfrac{w}{d \cdot W}$, where w and W are weights, and d is a temperature difference. It will be seen from this, that taking each factor, w, W, and d separately, the influence of each on the result is the same. But w and W can be measured with much greater accuracy than d, so that if the relative error in d is, say, 2 per cent., it will not be necessary to determine w and W with a greater accuracy than 0·2—0·4 per cent. If, therefore, w is about 0·5 g., and W about 20 g., the former need not be weighed to less than 1 mg., nor the latter to less than about 2 cg.

When the relative error of one of the factors is not considerably greater than that of the other factors, the latter have also their influence on the accuracy of the final result, and it can be shown that the square of the relative error in the final result is equal to the sum of the squares of the relative errors of the individual measurements.

Thus, for the determination of the specific rotation of an optically active substance, one has the formula (Chap. VII) $[\alpha] = \dfrac{\alpha}{l \cdot c}$. Suppose that the error in the determination of $\alpha = 0·05$ per cent.; in the determination of l, 0·01 per cent.; in the determination of c, 0·02 per cent. Then the error produced in the final result will be equal to $\pm \sqrt{(0·05)^2 + (0·01)^2 + (0·02)^2} = 0·055$ per cent. In accordance with what was said before (p. 8), the error 0·01 per cent. may be neglected in comparison with the error 0·05 per cent.

Determination of the Error of Observation.—One point still remains. The effect of a given error of observation on the final result has been considered, and one has now to ask how, in experimental work, the error involved in a given determination is gauged.

The simplest method which may be employed for this purpose is the determination of the average deviation of each observation of a series from the general mean. Thus, in determining the angle of rotation of an optically active substance, the following values were successively read : 27·84°,

27·83°, 27·84°, 27·80°, 27·82°, 27·84°. The mean of these numbers is 27·828°. The deviations of the individual readings from the mean are (neglecting sign) : 0·012, 0·003, 0·012, 0·028, 0·008, 0·012. The sum of the six numbers is 0·075 ; and the average deviation is therefore 0·012°. The error in the determination is therefore rather less than 1 in 2000, or about 0·05 per cent.

The result can be obtained more correctly with the help of the theory of probabilities. On the basis of this theory the mean error which may be taken as attaching to each determination is given by the expression

$$\pm\sqrt{\frac{\varSigma\delta^2}{(n-1)}}$$

where $\varSigma\delta^2$ is the sum of the squares of the deviations of the individual determinations from the mean, and n is the number of the determinations. Applying this in the above case, one obtains, for the *mean error of each determination*,

$$\pm\sqrt{\frac{12^2+3^2+12^2+28^2+8^2+12^2}{5}}=\pm16\cdot1$$

in units of the third decimal place ; or, the mean error of each determination is $\pm0\cdot016°$.

On p. 6 it was stated that the best representative value of a series of measurements is the arithmetical mean of the different values. To this mean value, however, is also attached an error, and the mean value of this error, or the *mean error of the mean*, is given by the expression

$$n(n-1)$$

In the case of the above series of measurements, therefore, the mean error of the mean is equal to

$$\pm\sqrt{\frac{12^2+3^2+12^2+28^2+8^2+12^2}{30}}=\pm6\cdot6$$

in units of the third decimal place, and this is indicated by writing the final value of the determinations in the form, 27·828°±0·007°. Increase in the number of separate measurements will diminish the value of this mean error of the mean, but does not diminish the value of the mean error of the individual determinations.

CHAPTER II

DETERMINATIONS OF WEIGHT AND VOLUME

BEFORE engaging on any physical measurement, it is of essential importance either to satisfy one's self that the different apparatus to be employed in the measurements are accurate, within definite limits, or to determine the errors attaching to the apparatus in order that the necessary corrections may be applied. The limit of accuracy which one can hope to attain will, of course, differ in the case of different instruments and apparatus, for all are not capable of the same degree of accuracy. It is necessary, therefore, to ascertain what is the degree of accuracy of each instrument or piece of apparatus. Since the apparatus for the determination of weight (or mass) and of volume are those most generally concerned, either directly or indirectly, in chemical or physico-chemical measurements, the methods of calibrating them may be considered first. The methods of calibrating other measuring instruments will be described as occasion arises.

THE BALANCE

The determination of the mass or weight [1] of a body is one of the most fundamental of physical measurements, and it is also one which is capable of a very high degree of accuracy. With a balance such as is employed in chemical analysis, it is not a matter of great difficulty to determine the weight of a body, weighing, say, about 100 g., with an accuracy of one part in one hundred thousand. In fact, the accuracy of the balance is in many cases greater than the accuracy with which a body can be defined or reproduced. Thus, in weighing vessels or apparatus of glass or other material before and after they have been used in an experiment, the difference in weight, due to the handling, the manner of

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[1] The weight of a body is proportional to the mass, being equal to the mass multiplied by the force of gravity. While the mass remains constant, the weight will vary with the place, since the force of gravity varies.

drying the apparatus, etc., may sometimes amount to at least several tenths of a milligram, while the accuracy of the balance itself might quite well allow of the weight being determined to less than one-tenth of a milligram.

After a balance has been placed in position and levelled, it should be tested with regard to its adjustment and its sensitiveness.

The first requirement which a balance must satisfy is that it shall be consistent with itself ; *i.e.* successive determinations of the weight of an object must be in agreement. From the closeness of agreement between the different weighings, the accuracy of the balance can be judged.

Determination of the Zero Point.—Before using the balance, and also from time to time during a series of weighings, the zero point, or the position of rest of the beam when unloaded, should be determined. This is done by releasing the beam and allowing it to swing free. Readings are then taken of the extreme points on the scale reached by the pointer on either side of the middle line ; two readings being made on one side of the middle line, and one on the other, the first swing being neglected. Suppose that the turning points on the right of the middle line were 6·0 and 5·5, while the turning point on the other side was 5·7 ; then the turning point on the right corresponding with the point 5·7 on the left is $\frac{6·0+5·5}{2}=5·8$. The corresponding turning points are therefore equidistant from the middle line, and the zero point is therefore correct.

On the other hand, suppose that the following turning points were observed, the readings to the right being called positive and those to the left negative—

$$-4·5 \qquad\qquad \begin{array}{l} +6·0 \\ +5·5 \end{array}$$

then the turning point on the right corresponding to that on the left is $\frac{+6·0+5·5}{2}=+5·8$, and the resting point is therefore $\frac{+5·8-4·5}{2}=+0·7$; *i.e.* the zero is 0·7 division to the *right*. Or again, suppose the turning points to be—

$$-6·5 \qquad\qquad \begin{array}{l} +5·0 \\ +4·6 \end{array}$$

then the corresponding turning points are $-6\cdot5$ and $+4\cdot8$, and the zero is therefore $\dfrac{+4\cdot8-6\cdot5}{2}=-0\cdot9$; *i.e.* $0\cdot9$ of a division to the *left* of the middle line.

Rule.—To find the position of rest, take the mean of the two readings on the one side, and divide the *algebraic* sum of this mean and the reading on the opposite side of the middle line by 2 ; the result gives the scale division corresponding to the resting point, and the sign ($+$ or $-$) indicates on which side of the middle line the zero lies.

Two or three determinations of the zero point should be made, and the mean taken. With a good balance the different determinations should not differ by more than one or two tenths of a scale division.

Unless the zero point is considerably removed from the middle line, the adjustment of the balance need not be altered ; but if it should be in excess of one scale division, the zero point should be corrected by means of the small screws at the ends of the beam, or of the metal flag which is above the centre of the beam.

Sensitiveness of a Balance. Weighing by Oscillations.—In determining the weight of a body, weights to the nearest centigram are placed on the scale-pan of the balance, and the milligrams and fractions of a milligram then determined by means of the rider. The fractions of a milligram can, however, be determined more accurately by the method of oscillations. As this depends on the sensitiveness of the balance, the latter must first be determined.

By the *sensitiveness* of a balance is meant the displacement of the resting point of the beam produced by an excess of 1 mg. on either side of the balance. The sensitiveness varies with the load on the balance, although, as a rule, not to any great extent, and should be determined, therefore, with different weights in the scale-pans. To obtain the sensitiveness of a balance, place on one side of the balance a given weight, and counterpoise it to within 1 mg. by means of weights and rider. Determine the resting point by the method given above. Now alter the position of the rider by an amount corresponding to 1 or 2 mg., in such a direction that the resting point is now on the other side of the zero point. The sensitiveness is then given by dividing the number of scale divisions between the two resting points by the difference of weight in milligrams.

EXAMPLE.—Suppose that with the weight of 10·354 g. the resting point is found to be +1·2 ; and with the weight 10·355 g. the resting point is −0·8. Then, the displacement of the resting point by a difference of weight of 1 mg. is 2·0 scale divisions ; and the sensitiveness is therefore 2·0 scale divisions for a load of 10 g.

The sensitiveness can be increased or diminished by raising or lowering the centre of gravity of the swinging parts of the balance by means of the so-called gravity bob, with which the better balances are furnished. Increase of sensitiveness, however, entails increase in the time of swing, and should not be carried too far.

Having determined the sensitiveness of a balance at a number of different loads in the above manner, the operation of weighing can be shortened, because it is only necessary to adjust the weight to the nearest milligram, and to determine the resting point, provided the zero point has been previously determined. The fractions of a milligram can then be calculated from the difference between the resting point with a given weight and the zero point, and from the sensitiveness of the balance.

EXAMPLE.—Suppose that the zero point of the balance is +0·5, the resting point with the weight 10·354 g., +1·2, and the sensitiveness 2·0 scale divisions. Then the additional weight required is $\dfrac{1\cdot2-0\cdot5}{2}=0\cdot35$ mg. The correct weight is therefore 10·35435 g.

The weight has here been expressed to five places of decimals, but whether or not the last place has any meaning will depend on whether the weight of the object which is being weighed remains constant to within one or two hundredths of a milligram. If it may vary by some tenths of a milligram, it will evidently be absurd to state the weight to five places of decimals. To weigh correctly to one or two units in the fifth decimal place demands experience and great care, so that in ordinary work a greater accuracy than one or two units in the fourth place of decimals cannot be expected.

In all cases where only differences in weight are in question, a slight inequality in the length of the arms of the beam will have no influence, provided the object to be weighed is always placed on the same side of the balance. This, of course, should be made a rule.

It should be unnecessary to emphasize here that accurate

weighings can be expected only if the balance is kept clean and free from dust, and if the beam is released and arrested in such a manner as not to cause jarring of the knife-edges. The beam must never be released with a jerk, and should be arrested only when the pointer is passing the middle point of the scale. The balance, also, should not be exposed to unequal heating, and should not, therefore, be placed in a window exposed to direct sunlight.

Calibration of Weights.—Even after the adjustment and accuracy of the balance have been tested in the manner described above, the accuracy of the weighings will still depend on the accuracy of the weights employed. Before undertaking accurate weighings, therefore, it is necessary to determine the errors in the weights ; and even in cases where great accuracy is not aimed at, a set of weights should always be calibrated, for errors of quite appreciable magnitude are sometimes found, even in expensive sets.

The method usually employed for the calibration of weights, and the one to be described first, is that due to Kohlrausch. It will be assumed that the set of weights consists of the following pieces—50, 20, 10′, 10″, 5, 2, 1′, 1″, 1‴ g. weights and corresponding fractional parts.

Having determined the zero of the balance, the 50-g. weight is compared with the sum of the others. In order to determine the ratio of the balance arms the method of double weighings is employed ; and the resting point is always determined by the method of oscillations.

Place the 50-g. weight on, say, the left scale-pan, and the weights from 20 g. downwards on the right, and determine what weight, if any, must be added to the weights on the right or left in order to give exact counterpoise, *i.e.* in order that the resting point coincides with the zero point of the balance. Now interchange the weights, placing the 50-g. weight on the right and the other weights on the left, and determine what weight must now be added to the left, or right, in order to obtain exact equipoise. In this way one obtains the two results—

Left.	Right.
50	$20+10'+10''+5+2+1'+1''+1'''+r$ g.
$20+10'+ \ldots +l$ g.	50

From these two weighings there is obtained as the relation

between the 50-g. weight and the sum of the smaller weights,

$$50 = 20 + 10' + 10'' + \ldots + \tfrac{1}{2}(r+l).^1$$

If, however, the ratio of the balance arms,[2] $\dfrac{R}{L}$, is known, then only one weighing is necessary, because, from the theory of levers, a weight w placed on the right pan is equivalent to a weight $w \times \dfrac{R}{L}$ on the left. Thus, suppose that the ratio $\dfrac{R}{L} = 1 \cdot 000009$, and suppose that it has been found that

$$50 \text{ g. (standard)} = 50 + 0 \cdot 0001$$

then,

$$50 \text{ g.} - 0 \cdot 0001 = 50 \times 1 \cdot 000009 = 50 + 0 \cdot 00045$$

Therefore the true value of the 50-g. weight is—

$$50 \text{ (standard)} - 0 \cdot 00055 = 49 \cdot 9995 \text{ g.}$$

As the value of the ratio $\dfrac{R}{L}$ varies slightly with the load, it should be determined with different loads—say with 50 g. and with 20 g. on each scale-pan. The value found in the second case can then be used for the smaller weights, for in general the correction is so small as to be negligible.

---

[1] This expression can readily be deduced from the theory of levers. If R and L represent the lengths of the balance arms, then—

$$50L = (20 + 10' + 10'' + \ldots + r)R \quad \ldots \quad \text{(i)}$$
$$= (S + r)R$$

where $S = 20 + 10' + \ldots + 1'''$.

$$\text{Also, } (S + l)L = 50R \quad \ldots \quad \ldots \quad \text{(ii)}$$

Combining these two equations one obtains—

$$50^2 LR = (S + r)(S + l)LR$$
$$= [S^2 + S(r + l) + rl]LR$$

Neglecting rl, the product of two small quantities, one obtains—

$$50^2 = S^2 + S(r + l)$$
$$\text{or, } 50 = S + \tfrac{1}{2}(r + l) \text{ (approximately)}$$
$$= 20 + 10' + 10'' + \ldots + \tfrac{1}{2}(r + l)$$

[2] The ratio of the balance arms can be obtained from equations (i) and (ii) above. Thus, $\dfrac{R}{L} = \dfrac{50}{S+r} = \dfrac{S+l}{50} = \dfrac{S+l+50}{S+r+50} = \dfrac{100+l}{100+r}$ (approximately)

$= 1 + \dfrac{l-r}{100}$ (approximately).

One proceeds, in the manner described above, with the comparison of the other weights among themselves, comparing the 20-g. weight with the sum of $10'+10''$, $10'$ with $10''$, 10 with the sum of $5+2+1'+1''+1'''$, 2 with $1'+1''$, $1'$ with $1''$ and with $1'''$.   Similarly with the fractions of a gram. In this way the relative values of the different weights are obtained, and if the exact value of any one of the pieces (by comparison with a standard weight) is known, the correct values of the other pieces can be calculated.

The following example will make the method quite clear.   The weighings should be made to the fifth place of decimals by the method of oscillations.   In the example below, the numbers have been rounded off to the nearest tenth of a milligram.[1]

EXAMPLE :—

1. $\quad$ 50 g. (standard) $=50+0\cdot0001$
$\qquad$ $50+0\cdot0010$ $\quad$ $=50$ g. (standard)
$\quad$ hence $\quad$ 50 g. (standard) $=50+\frac{1}{2}(0\cdot0010+0\cdot0001)$
$\qquad\qquad\qquad\qquad\quad$ $=50+0\cdot0005$
$\qquad$ Therefore $\quad$ $50=\underline{49\cdot9995}$ g.
$\qquad\qquad$ Also, $\dfrac{R}{L}=1\cdot000009$

2. $\qquad$ $50+0\cdot0057=20+10'+10''+$etc.
$\qquad$ $20+10'+10''+\ .\ .\ .\ =50+0\cdot0049$
$\qquad$ hence $50=20+10'+10''+\ .\ .\ .\ -0\cdot0053$
$\qquad\qquad$ and $\dfrac{R}{L}=1\cdot000008$

3. $\qquad\qquad$ $20=10'+10''+0\cdot0017$
$\quad$ $10'+10''+0\cdot0018=20$
$\qquad\qquad$ hence $20=10'+10''+0\cdot0018$

$\qquad\qquad$ and $\dfrac{R}{L}=1\cdot000001$

4. $\qquad\qquad$ $10'=10''+0\cdot0002,\ \dfrac{R}{L}=1\cdot000001$
$\qquad$ $\therefore\ 10'=10''+0\cdot0002$

5. $\qquad$ $10'+0\cdot0022=5+2+1'+1''+1'''\ \left(\text{Neglect }\dfrac{R}{L}\right)$
$\qquad\qquad$ $\therefore\ 10'=5+2+1'+1''+1'''-0\cdot0022$

6. $\qquad\qquad$ $5=2+1'+1''+1'''-0\cdot0026$

and so on.

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[1] Where the highest degree of accuracy is desired, the fifth decimal place should be retained throughout the whole series of calculations, and the values rounded off to the fourth decimal place only at the end of the operation.

By comparison with the standard weight it was found that the piece marked 50 has the mass 49·9995 g.

From weighing (2), therefore, it is found—

$$49·9995 \text{ g.} = 20 + 10' + 10'' + \ldots -0·0053$$
$$\text{or, } 20 + 10' + 10'' + \ldots = 50·0048 \text{ g.}$$

But from the relationships found above, one can write—

$$20 + 10' + (10' - 0·0002) + (10' + 0·0022) = 50·0048 \text{ g.}$$
$$\text{or } 20 + 10' + 10' + 10' = 50·0028 \text{ g.}$$
$$\text{Further, } 20 = 10' + 10'' + 0·0018$$
$$= 10' + (10' - 0·0002) + 0·0018$$
$$= 10' + 10' + 0·0016$$

Hence $(10' + 10' + 0·0016) + 10' + 10' + 10' = 50·0028$ g.

$$\text{or } 5 \times 10' = 50·0012 \text{ g.}$$
$$\text{therefore } 10' = 10·0002 \text{ g.}$$
$$\text{and } 10'' = 10·0000 \text{ g.}$$
$$20 = 20·0020 \text{ g.}$$

and similarly with the lower weights.

The necessity of taking account of the ratio of the length of the balance arms and of interchanging the weights from one scale-pan to the other can be avoided, and the work of standardization simplified, by using the method of substitution. For this purpose a tare [1] is placed on the right-hand scale-pan and the standard weight on the left, and the resting point determined. If this differs greatly from the zero point of the scale, the rider should be used in order to bring the resting point to within 1–1·5 scale divisions of the zero.[2] Having determined the resting point with the standard weight, the latter is replaced by the weight to be standardized, and the rider then moved, if necessary, so that the same resting point is obtained as with the standard weight. (Here also the method of oscillations should be employed.) In this way, the relation between the standard weight and the weight to be standardized is at once obtained. In the same way, also, the different weights may be compared with one another. Their correct values can then be calculated as before.[3]

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[1] As a tare one may use most suitably the appropriate piece from another set of weights.

[2] In order to diminish the error of reading, it is best so to arrange matters that the rider is used only in the middle third of the balance arm. To ensure this a weight of 5 mg. should be kept throughout the whole operation of standardization on the *left hand* scale-pan.

[3] For methods of standardizing weights, see also Richards, *J. Amer. Chem. Soc.*, 1900, **22**, 144; Hopkins, Zinn and Rogers, *ibid.*, 1920, **42**, 2528; Blade, *Ind. Eng. Chem. (Anal.)*, 1939, **11**, 499.

If a complete set of standardized weights is available, then each weight in a set can be calibrated in the manner described above for the 50 g. weight.

Correction for the Buoyancy of the Air.—In exact determinations of the weight of a body, the apparent weight, *i.e.* the sum of the face values of the weights used (corrected as described above) must be corrected for the buoyancy of the air ; for a body will appear lighter by an amount equal to the weight of the air displaced. The greater the difference in the density or the specific volume of the body and the weights used to counterpoise it, the greater will be the correction.

If a body of the density d is counterpoised by brass weights of the value G g., the volume of the body will be $\dfrac{G}{d}$ ml., and its weight will therefore be diminished by $\dfrac{0\cdot0012G}{d}$ g., where 0·0012 g. is the weight of 1 ml. of air under ordinary conditions (mean room temperature, normal pressure, and average humidity). The true weight of the body would therefore be $\left(G+\dfrac{0\cdot0012G}{d}\right)$ g., if the true weight of the counterpoise were G g. But the brass weights by which the body is counterpoised have a volume equal to $\dfrac{G}{8\cdot5}$ ml., where 8·5 is the density of brass ; and they therefore suffer a diminution in weight of $\dfrac{0\cdot0012G}{8\cdot5}$ g. The true weight,[1] G_0, of the body is therefore equal to $G+\dfrac{0\cdot0012G}{d}-\dfrac{0\cdot0012G}{8\cdot5}$, or $G_0=G\left(1+\dfrac{0\cdot0012}{d}-\dfrac{0\cdot0012}{8\cdot5}\right)=G\left(1+\dfrac{0\cdot0012}{d}-0\cdot00014\right)$. In order, therefore, to obtain the true weight (*i.e.* the weight which the body would have in a vacuum) of a body weighed in air with brass weights, one must *add to each gram apparent weight* (G) the quantity $\left(\dfrac{0\cdot0012}{d}-0\cdot00014\right)$ g. The following table given by Kohlrausch gives the value of this correction in milligrams for different values of d :—

[1] See also p. 65.

d	Correction.	d	Correction.	d	Correction.
0·7	+1·57	2·0	+0·457	9	—0·010
0·8	+1·36	2·5	+0·337	10	—0·023
0·9	+1·19	3·0	+0·257	11	—0·034
1·0	+1·06	3·5	+0·200	12	—0·043
1·1	+0·95	4·0	+0·157	13	—0·051
1·2	+0·86	4·5	+0·124	14	—0·057
1·3	+0·78	5·0	+0·097	15	—0·063
1·4	+0·71	5·5	+0·075	16	—0·068
1·5	+0·66	6·0	+0·057	17	—0·072
1·6	+0·61	6·5	+0·042	18	—0·076
1·7	+0·56	7·0	+0·029	19	—0·080
1·8	+0·52	7·5	+0·017	20	—0·083
1·9	+0·49	8·0	+0·007	21	—0·086

CALIBRATION OF VOLUMETRIC APPARATUS

By international agreement, the unit of volume is the *litre*, which is defined as the volume occupied by 1 kilogram of pure water at the temperature of maximum density and under normal atmospheric pressure, the weight being reduced to vacuum. Although, originally, the mass of 1 kg. was intended to be the mass of 1 cubic decimetre or 1,000 cubic centimetres (cm.^{3}) of water at its temperature of maximum density and under normal atmospheric pressure, actually the kilogram is now simply the mass of the " kilogramme des Archives " preserved in Paris ; and since this mass is not exactly equal to the value as originally defined, the definitions of a litre and of a cubic decimetre are no longer directly related in theory. Experimentally, one finds, 1 litre=1,000·028 cm.^{3}, or 1 cm.^{3}=0·00099973 litre. The thousandth part of a litre, a *millilitre* (ml.) is equal to 1·000028 cm.^{3}

For a considerable time, volumetric apparatus used in chemical and physico-chemical laboratories, has been graduated in terms of the volume of 1 gram of water at 4° c. and under normal atmospheric pressure, that is, in *millilitres*, but since the difference between the volume of 1 ml. and 1 cubic centimetre (cm.^{3}) is negligible for all practical purposes, excepting those demanding the highest degree of accuracy, the smaller unit of volume is frequently referred to as a cubic centimetre, and represented by c.c. Although all new volumetric apparatus is now graduated and marked in millilitres (ml.), there is still much apparatus in use which is graduated in millilitres but marked c.c. Whilst it

is advisable that the internationally accepted unit, millilitre, should be generally adopted, it must be understood that the term c.c. is frequently used as synonymous with ml. The volume of a true cubic centimetre, or the volume of a cube of 1 cm. side, is represented by cm.[3]

In order to determine a given volume, one determines the weight of a liquid, generally water (distilled), required to fill the volume, the weight being reduced to vacuum. To save the trouble of making this reduction, use can be made of the accompanying table, which gives the volume (in ml.)

Temperature.	Apparent weight of 1 ml. of water.	Volume corresponding with an apparent weight of 1 g. of water.
10°	0·9986	1·0013
11°	0·9985	1·0014
12°	0·9984	1·0015
13°	0·9983	1·0017
14°	0·9982	1·0018
15°	0·9981	1·0019
16°	0·9979	1·0021
17°	0·9977	1·0023
18°	0·9976	1·0024
19°	0·9974	1·0026
20°	0·9972	1·0028
21°	0·9970	1·0030
22°	0·9967	1·0033
23°	0·9965	1·0035
24°	0·9963	1·0037
25°	0·9960	1·0040

corresponding to an apparent weight of 1 g. of water (*i.e.* weight in air), and the apparent weight of 1 ml. of water, at different temperatures. The table applies only when the weighings are carried out with brass weights.

Calibration of Measuring Flasks.—For the purpose of measuring definite volumes of liquid, as, for example, in making solutions of definite concentration, flasks of various sizes, provided with fairly long necks, are employed. These should be fitted with accurately fitting, ground-in stoppers (hollow stoppers being preferable to those of solid glass), and are made so as to contain a definite whole number of ml. of a liquid when filled up to a ring marked on the neck. The bulb of the flask should be of such a size that the volume mark is near the lower end of the neck.

With regard to the width of the neck, this should be of such a size that the error in reading the volume is not greater than the allowable error in the calibration of volumetric apparatus, which may be taken as 0·05 per cent. of the volume measured. In the case of smaller flasks, for 50 ml. or less, the Regnault flask (Regnault pyknometer) is very useful. This has a very narrow neck, so as to diminish the error in reading; and in order to obtain sufficient air-space to ensure ready mixing, the neck is widened at the top (Fig. 1).

Although the flasks made by the best makers will, as a rule, be found sufficiently accurate, no flask should be employed for accurate work without being tested.
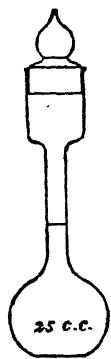

FIG. 1.

To calibrate a flask, the latter is first cleaned and thoroughly dried; it is then counterpoised on a balance, and distilled water, having a temperature of 15° to 18°, is run into the flask until the lower edge of the meniscus stands at the level of the volume mark on the neck. Any water which may have got on the neck above the mark should be removed by means of filter paper. The weight of the water is then determined. (For flasks having a volume of 200 ml. upwards, the weighings should be carried out on a balance which need not be accurate to less than a centigram; in the case of smaller flasks, the weighing must be done on a more sensitive balance.)

The weight of water contained in the flask up to the mark having been determined, the volume can be obtained from the table given on the previous page. For example, since an apparent weight of 1000 g. corresponds to a volume at 17° of 1002·3 ml., the true volume of the flask is obtained from the expression $\frac{1002·3 \times w}{1000}$, where w is equal to the weights employed. If the error is at all considerable, a second ring, corresponding to the volume of 1000 ml. (or other volume, according to the flask), should be etched on the neck.

It may also be necessary sometimes to graduate a flask for one's self. In this case the flask, after being cleaned and dried, is counterpoised on a suitable balance; the necessary weights are placed on the scale-pan, and distilled water is then poured into the flask until equipoise is obtained. In this case the last few millilitres should

be introduced by means of a pipette, any drops of water which may have formed on the upper part of the neck being first removed by filter paper. Since from the table one learns that the apparent weight of 1 ml. of water at 17° is 0·9977 g., the weights necessary for any given volume can be calculated.

After the necessary amount of water has been introduced into the flask, the latter is placed on a level table, and a strip of gummed paper is then fixed round the neck, so that its upper edge coincides with the lower edge of the water meniscus. The water is then emptied from the flask, and the neck coated with a thin, uniform layer of paraffin wax, extending some distance on either side of the gummed paper. When the wax has become cold, a ring is cut by means of a knife along the upper edge of the gummed paper. The exposed glass is then etched by means of hydrofluoric acid, the acid being rubbed into the cut in the wax by a little mop of cotton-wool wound round the end of a stout copper wire.

Calibration of Pipettes.—Pipettes are calibrated by weighing the water which they deliver. In carrying out the calibration, however, several precautions must be observed if an accuracy of 0·05 per cent. is to be obtained.[1] In the first place, it must be seen that the glass of the pipette is free from all greasiness, so that the water runs from the pipette without leaving drops behind. If necessary, therefore, the pipette must first be thoroughly cleaned. This is best effected by filling the pipette several times with a warm solution of potassium dichromate strongly acidified with concentrated sulphuric acid ; or the pipette may be left for some time full of the acid dichromate mixture.[2]

FIG. 2.

If the liquid is sucked up by mouth, care must be taken not to suck the solution into the mouth. As this sometimes happens, owing to the end of the pipette being inadvertently raised above the level of the solution, it is wise to attach to the end of the pipette a safety tube of the form shown in Fig. 2.

Again, attention must be paid to the way in which the pipette is allowed to deliver, and also to the time of delivery. The pipette should be held upright or, in any case, not

[1] For an investigation of the methods of calibration and accuracy of pipettes and burettes, see Wagner, *Z. physikal. Chem.*, 1899, **28**, 193.

[2] When not in use, pipettes should be kept standing in a tall cylinder full of the dichromate solution, or be laid, filled with the dichromate solution, in a horizontal position ; the glass will in this way be prevented from becoming greasy. The pipette is then rinsed out two or three times with distilled water before use.

sloping at an angle greater than 45°, and the liquid allowed to run out freely. Immediately the liquid stops running, touch the point of the pipette momentarily against the side of the vessel, so as to remove the drop of liquid which collects at the point, and then withdraw the pipette. The pipette, also, must not be allowed to deliver too rapidly, otherwise varying amounts of liquid will be left adhering to the sides, and, consequently, the volume delivered will vary. The time of outflow must therefore be regulated so that the time required for the delivery of a pipette of 10 ml. capacity, or over, is from 40 to 50 seconds. This can be effected by partially closing the end of the pipette in the Bunsen flame.

Having cleaned and regulated the time of outflow of the pipette, the position of the mark on the stem is first determined approximately. To do this, a mark is made on the stem with a pencil for writing on glass, or with ink ; distilled water is drawn up to this mark, and then allowed to flow into a previously weighed stoppered or corked flask, and the weight of water determined. According as this weight is greater or less than the desired amount, a strip of gummed paper, with sharp cut edge, is placed round the stem of the pipette below or above the first mark ; water is sucked up into the pipette, its level adjusted to the sharp edge of the paper strip, and the weight of water delivered determined. If the correct position has not yet been obtained, another strip of paper is fixed round the stem, and another weighing of the water delivered is made. Some idea of where this second strip must be placed will be obtained from the difference between the first two weighings and the distance of the two marks apart. The second strip should be fixed at such a point that the weight of water is on the opposite side of the correct weight from that given by the first strip ; *i.e.* if the former weight was too small, the second strip should be placed so as to give too great a weight. Having in this way determined two points on the stem of the pipette, such that the weight of water delivered is too great in the one case and too small in the other, the correct position of the mark can be calculated fairly accurately from the difference of the two weighings and the distance of the paper strips apart. A third paper strip should then be placed at the calculated point, and the correctness of the position tested by weighing the water delivered. Three concordant weights, the mean of which does not differ from the correct weight by more than

0·05 per cent., must be obtained. To obtain the correct weight, use is again made of the table on p. 21, in order to find the apparent weight corresponding to the volume desired. The temperature of the water used should be that of the mean room temperature, 15°.

The position of the mark on the stem having been determined, a ring is etched as explained on p. 23.[1]

For certain purposes (*vide* Chap. X.) pipettes are required to *take up* a definite volume of liquid. To calibrate a pipette for this purpose, a stoppered flask containing distilled water is weighed ; water is then drawn up to a mark on the pipette, and the amount thus withdrawn determined by reweighing the flask and water. The correct position of the mark on the pipette is determined by trial in the manner described above, and the correctness of the position tested by repeating the operation several times, as in the previous method of calibration. In order that the amount of water adhering to the walls of the pipette shall be as nearly as possible the same each time, the pipette should be placed in an upright position, with the point resting on filter paper, and allowed to drain for about five minutes.
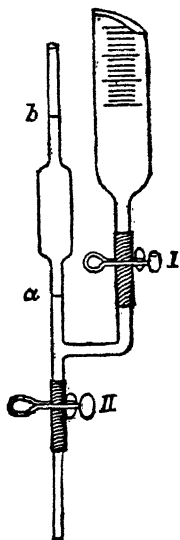
FIG. 3.   FIG. 4.

Calibration of Burettes.—Burettes are most simply calibrated by the Ostwald method with the help of a small pipette (generally 2 ml.), the volume of which has been accurately determined (Fig. 3). The calibration pipette is attached to the burette in the manner shown in the figure (Fig. 4). If the burette is furnished with a glass tap, the

[1] The calibration as carried out above is valid only for water and aqueous solutions. Where the pipette is to be used for other liquids, a redetermination of the volume of liquid delivered should be made by dividing the weight delivered by the density of the liquid at the particular temperature.

clip I is omitted.   The pipette may be kept in position by means of a loop of copper wire passing round the burette and the upper end of the stem of the pipette.

Before use, the burette and the pipette must first be thoroughly cleaned with dichromate and sulphuric acid (p. 23).   The pipette is then attached to the burette, and the latter filled full with water.   The clip I (or the stop-cock of the burette) is then opened so as to fill the side tube of the pipette and the lower part of the latter below the mark a, care being taken that all air-bubbles are driven out of the tubes.   The level of the water is then adjusted so that it stands at zero mark on the burette, and at the mark a on the calibration pipette.   The clip I is then carefully opened, and water allowed to flow from the burette until it reaches the mark b on the pipette.   A definite volume (say 2 ml.), is thus withdrawn from the burette, and the reading on the burette is compared with this.   The clip II is then opened, and water allowed to run from the pipette until it reaches the mark a, and is collected in a small flask which has been previously weighed.   The flask should be kept corked except while water is being run into it.   A further 2 ml. of water is allowed to run from the burette, and a reading again made ; clip II is again opened, and water allowed to run from the pipette until the level falls to a, the water being again collected in the weighed flask.   These operations are repeated until the water has been run down to the lowest mark on the burette.   The total weight of water thus run off is determined, and from this the volume of the calibration pipette is obtained.   Knowing the volume of the pipette, and the corresponding readings on the burette, the corrections for the latter are obtained.   Thus, suppose that the volume of the pipette was found correct, equal to 2 ml., and that the readings on the burette, after successive withdrawals of 2 ml., were 1·99, 3·96, 5·98, 8·02, 10·02, 11·98, etc., then the corrections to be applied at the points 2, 4, 6, 8, 10, 12, etc., ml. on the burette would be +0·01, +0·04, +0·02, −0·02, −0·02, +0·02, etc., and at any intermediate point, the correction may be taken as proportional to the corrections on either side of it.   These corrections for every 2 ml. may be written in tabular form ; but it is better, especially if the corrections are considerable, to draw a curve of corrections, the burette readings being represented as abscissæ, and the value of the corrections being represented

as ordinates above (for positive corrections) or below (for negative corrections) the abscissa axis. The correction values are then joined by straight lines, so that for any given reading on the burette the correction can be seen at a glance. Such a curve of corrections, plotted from the figures given above, is shown in the diagram (Fig. 5).

As with pipettes, so also in the case of burettes, attention must be paid to the rate at which the liquid is allowed to flow out. The minimum time of outflow advisable will depend on the volume of liquid delivered ; for 30 ml. it should be not less than about 40 seconds.

With burettes the accuracy to be attained is not in general so great as with pipettes, and will depend on the internal
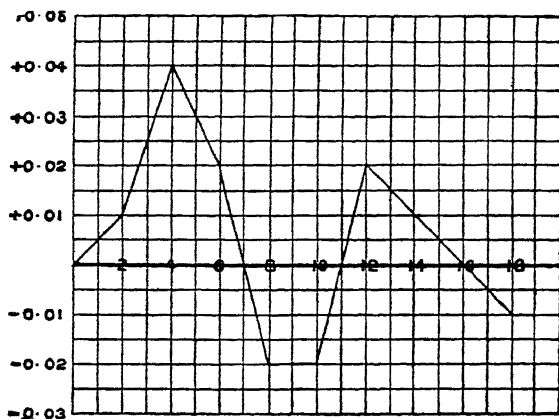
FIG. 5.

diameter of the burette. The latter should be as small as possible, consistent with convenience in length. For most purposes it is convenient to use a 30 ml. burette, the internal diameter of which should be from 8–10 mm. With such burettes an accuracy of about 0·1 per cent. can be obtained on a reading of 10 ml.

Parallax.—In making a reading of volume by means of a burette, it will be found that as the line of vision is raised or lowered, the apparent position of the liquid meniscus alters. Owing to this apparent change of position, to which the term *parallax* is applied, such volume readings are liable to considerable errors. These can be avoided most easily by placing a piece of mirror glass behind the burette, and then

raising or lowering the line of vision until the meniscus and its image just coincide. The eye is then on the same level as the meniscus, and the error due to parallax disappears. The reading is then made with the eye in this position. Burettes can also be obtained on which the main divisions are engraved completely round the burette. With such burettes errors of parallax are readily avoided.

It will be clear that the precautions to be taken in reading a burette should also be taken when using apparatus of a similar character, *e.g.* the barometer, eudiometer, mercury manometer, etc.

CHAPTER III

THERMOSTATS

As very many of the measurements in physical chemistry are markedly affected by temperature, it is necessary to have some means whereby experiments can be carried out at constant temperature. Constant temperature baths, or *thermostats*, are, therefore, a very important part of the equipment of a physical chemical laboratory.[1]

The method employed for obtaining a constant temperature will, of course, depend largely on the temperature required. Occasionally, changes of physical state, *e.g.* fusion and vaporization, in which the temperature is maintained constant by the process itself, can be employed with advantage ; more especially is this the case when boiling liquids can be used. This method finds its chief application when the apparatus can be entirely surrounded by a jacket filled with the vapour of the boiling liquid, *e.g.* in the Victor Meyer or Lumsden apparatus for the determination of vapour densities (p. 51). The method has the disadvantage that one is bound more or less to certain fixed temperatures ; for although variations can be obtained by artificially controlling the pressure under which the liquid boils, the apparatus thereby becomes much more complicated.

The melting of substances may also be used to produce constant temperatures, and in this connection the substance most commonly employed is ice. If a temperature of 0° is desired, ice can be used, but it must be pure. It is therefore best to employ the ordinary ice to surround a vessel containing partially frozen distilled water.

In a similar manner other temperatures dependent on the existence of invariant systems can be obtained, *e.g.* cryohydric temperatures and transition temperatures of certain salt hydrates. (See Table I., Appendix.)

In by far the largest number of cases, however, constant temperatures are obtained by means of liquids, more

[1] See Thorpe's *Dictionary of Applied Chemistry.*

especially of water, the regulation of the temperature being effected by methods to be described below.

The Bath.—The vessel for the constant-temperature liquid may vary, both as regards size and material, according to the purpose for which it is to be employed.   For most purposes enamelled iron vessels are exceedingly convenient ; or one may also use copper, aluminium, stainless steel, or galvanized iron baths, which are everywhere obtainable at a small price. In the case of the last-mentioned, the inside of the bath should be painted with a good white enamel paint.   In all cases it is wise to surround the outside of the bath with felt.

For some purposes, *e.g.* measurements of viscosity, it is necessary to have a transparent bath, or at least a bath with one of its sides transparent.   In this case, a large beaker will often serve the purpose admirably.   Or, if the temperature required is not very high, an inverted glass bell-jar can also be used ; but in general a metal bath fitted with glass sides will be preferred.

As *bath liquid,* the most convenient is, of course, water.[1] This can be used for all temperatures up to near its boiling-point ; but when the temperature employed is higher than about 50°, it is well to cover the surface of the water with a layer of olive oil, to prevent evaporation.   The presence of this is, however, always more or less objectionable, and it can in general be dispensed with if a constant level apparatus is employed.   For temperatures over 100° and up to 140°-150°, a concentrated solution of calcium chloride can be employed.

Constant Level Apparatus.—A simple constant-level device can readily be made and used with any water bath.   The apparatus is constructed of glass tubing fitted together as shown in Fig. 6.

Before being used, the tubes E, F. and D are filled with water ; and after the tube B has been filled with water up to the end of the waste-pipe C, water will syphon off from B into the thermostat W, until the level of the water in the latter rises to that in the tube B.

The tube E, it may be mentioned, is necessary in order to act as an air-trap.   By this means the blocking of the

[1] When water is used as bath liquid, a slimy growth is apt to form after some time.   To prevent this, suspend in the bath a muslin bag containing mercuric iodide ; or dissolve a little mercuric chloride in the water.

syphon tubes by air-bubbles given off from the water is prevented. When too much air begins to collect in E, it can be removed by sucking through the rubber tube G, which is ordinarily closed by means of a screw-clip or by a glass tap.

Regulation of the Temperature.—The means to be adopted for securing a constant bath temperature will depend on

FIG. 6.

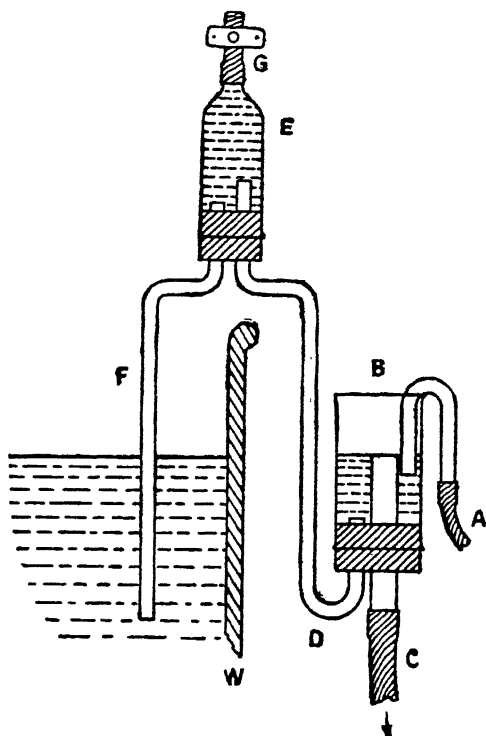whether the desired temperature is above or below that of the surroundings.

1. *Temperature above that of the surroundings.*—When it is desired to maintain a temperature above that of the surroundings, heat must be added to the bath to make up for the loss by radiation, evaporation, etc. This may be effected by means of a gas flame or, preferably, by means of an electric heater. The size of the gas flame, or the current

supplied to the heater, is automatically regulated by means of a *thermo-regulator*.

(*a*) *Gas heating.*—Various forms of regulators for gas heating have been introduced, one of the forms most suitable for ordinary purposes being shown in Fig. 7. This regulator may be used when the vessel is not too large, and when the bath liquid is efficiently stirred. The wide end of the tube A is filled with toluene (on account of its considerable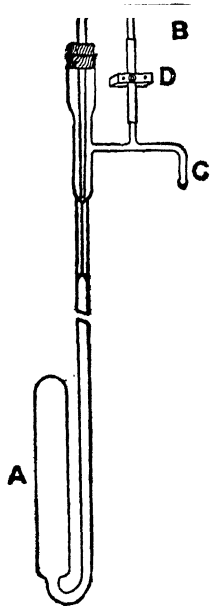 thermal expansibility and its fairly high boiling-point), while the bend and the narrow upright tube are filled with mercury. The upper end of the tube is of small bore, in order to increase the sensitiveness of the regulator by giving a relatively large rise and fall of the meniscus for a given change of volume of the toluene. The gas passes in through the tube B, which is fixed by means of a cork in the upper expanded end of the regulator tube, and thence through the side tube C to the burner. If the temperature of the bath should rise too high, the toluene expands and raises the surface of the mercury in the narrow tube, thus closing the end of the inlet tube B, and cutting off the gas supply. In order that the flame may not be completely extinguished, there is a side tube D (a by-pass), of indiarubber, through which gas passes directly to the burner. The clip on the rubber tube should be regulated so that the amount of gas which passes when the end of B is closed by the mercury, is just insufficient to maintain the thermostat at the desired temperature. When the end of the tube B is closed, therefore, through the rise of the mercury, the flow of heat to the thermostat will be diminished ; the temperature will fall, the toluene will contract, the mercury meniscus will fall and so open the end of B again, and allow a larger supply of gas to pass. By means of this regulator, therefore, there will be a fluctuation of temperature about a certain mean value ; but if the regulator is working properly, the fluctuation should not exceed 0·05°.

FIG. 7.

The regulator is first filled with pure toluene by allowing the liquid to flow into the previously evacuated tube, and then, by alternate heating and cooling, mercury is filled in in such amount that it fills the narrow upright tube and forms a layer 1·5–2 cm. deep in the wide tube A. Any toluene which may have collected on the upper surface of the mercury must be removed by means of a plug of cotton-wool, or by means of filter paper.

The quantity of mercury must now be roughly adjusted for the temperature at which the regulator is to be used. For this purpose, the regulator is placed in a bath of water at the desired temperature for several minutes. If too much mercury has been introduced, the excess is removed by means of a pipette until the mercury meniscus occupies the lower end of the tube above the capillary. If too little mercury has been introduced, then the regulator should be placed in a beaker of warm water so that the surface of the mercury rises above the end of the capillary, and a further quantity of mercury should then be poured in. The regulator is then placed in the bath again and the level of mercury adjusted. The exact adjustment is carried out by means of the inlet tube B. The adjustment of the mercury level can also be effected by means of a screw working in a side tube as in Fig. 16 (p. 41).

For gas heating, up to a temperature of about 30°, a small burner giving a luminous flame may be used and the flame should be protected from draughts by means of a cylinder of quartz glass or mica. For higher temperatures, the large luminous flame necessary to maintain the temperature will give rise to too much soot. It is therefore better to supply most of the heat to the thermostat by means of a Bunsen flame which is so regulated that, by itself, it maintains the temperature about a degree below that desired. The maintenance of the desired temperature is then effected by means of the small luminous flame attached to the regulator. Whenever a Bunsen flame is used, a gauze cap or a rose top should be placed on the end of the tube to prevent the flame from striking back. To obviate the risk of fire through the perishing or destruction of rubber, connection of the burner with the gas main should be made by means of metal tubing.

In order to maintain a uniform temperature throughout the bath, the water should, in all cases, be kept in motion by means of an efficient stirrer.

(b) *Electrical heating and control.*—When electric current is available, it is best to use electricity for the purpose of heating the thermostat, the current being passed through a heating resistance immersed in the water of the thermostat. As heating element one can employ either one or

more incandescent electric lamps,[1] or insulated immersion heaters such as are now put on the market in various forms. The heating resistance is best connected with the main lighting or power circuit, and is controlled by means of a relay in conjunction with a thermo-regulator.[2]   The general arrangement is shown in Fig. 8.

For the purpose of regulating the heating current, the toluene-mercury regulator, modified as shown diagrammatically in Fig. 9 can be employed.   A platinum wire, a, is sealed into the stem of the regulator so as to make contact
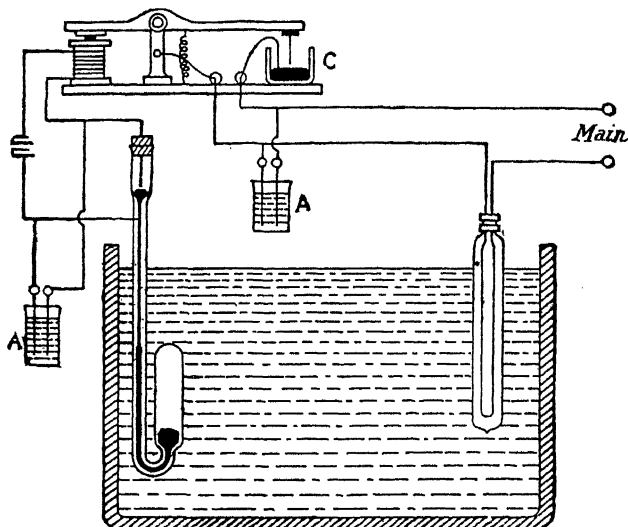
FIG. 8.

with the mercury, while a second platinum wire, b, is supported in the mouth of the regulator.   These two platinum wires are connected with a small battery through

[1] For this purpose one can employ lighting lamps made with a long glass stem so as to allow the globe to be completely immersed in the water of the thermostat, or the ordinary lamp and holder can be used, provided the latter is suitably protected from the water.   Instead of lighting lamps one may preferably employ a long-globed lamp such as is used for electric radiators.

[2] It will generally be advisable to have two heating elements in the bath.   One of these is connected directly with the main through a suitable resistance, and the current is regulated so that the heater maintains the temperature of the bath at slightly below the desired value.   The second heater is controlled by the thermo-regulator.

the coils of an electro-magnetic relay and through a sliding resistance adjusted so as to give a current just sufficient to work the relay. When the mercury rises in the regulator, owing to rise of temperature in the bath, contact with the upper platinum wire is made and the electric circuit through the coils of the relay is closed. The end of the beam of the relay (Fig. 8) is attracted and the heating circuit broken at the mercury cup C. When the bath cools down, the contact between the mercury of the regulator and the upper platinum wire, and consequently the current through the coils of the relay, are broken ; the beam of the relay is pulled down by the spring and contact again made at the cup C, whereby the heating circuit is again closed.

In order that the apparatus described above shall work satisfactorily over a lengthened period of time, the platinum-mercury contacts must be kept clean ; and sparking at these points must therefore be prevented. This can be effected to a large extent by inserting a suitable condenser A (about 0·5 microfarad) across the spark-gaps.[1] It is advantageous, also, to keep the mercury of the thermo-regulator in a state of tremor, so as to prevent sticking between mercury and platinum. Sufficient tremor can generally be obtained by attaching both stirrer and regulator to the side of the thermostat.

A thermo-regulator, more convenient to use and more sensitive in its action than that represented by Fig. 9, has been devised by B. Jelinek.[2] The upper part of this regulator which, when in use, is immersed

FIG. 9.

in the bath liquid, is shown in Fig. 10, from which its action will be readily understood. In place of toluene, paraffin oil (medicinal paraffin), contained in a branched bulb of about
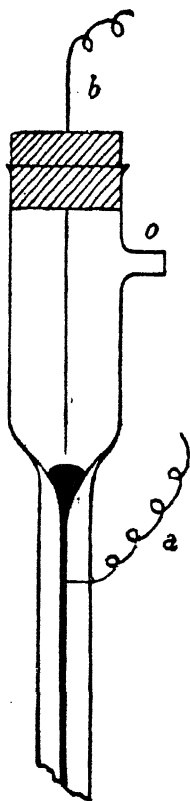
[1] For this purpose, two aluminium plates immersed in distilled water may be used. The mercury in the cup C may also be covered with a layer of glycerin.

[2] *Bull. Soc. Chim.*, 1937 (v.), **4**, 1811.

150 ml. capacity, is used as regulating liquid and fills also the upper part of the regulator above the mercury. While the regulator is being adjusted for temperature, tap C is
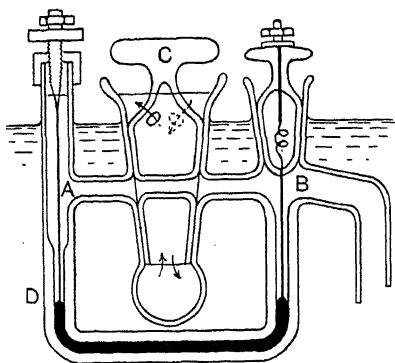
FIG. 10.

kept open so that oil can expand into A without affecting the level of the mercury; and when the desired temperature is reached, tap C is closed. Rise of temperature and expansion of the paraffin oil then cause the mercury to make contact with the platinum or steel needle at D. The circuit through the relay is thereby closed, and the heating current interrupted. The adjustment of this regulator for different temperatures is rendered very simple by means of the tap C, and the complete immersion of the regulator in the bath liquid renders its

functioning independent of the surrounding atmospheric temperature.

Instead of the relay shown in Fig. 8, one may use the relay [1] shown in Fig. 11, where contact is made between two silver studs. When current passes through the electro-magnet coils, the iron tongue T is attracted, the extent of its movement being regulated by the insulated screw S. When current ceases to pass through the coils, the iron tongue falls and contact is made between a silver stud in the tongue and a silver point

FIG. 11.

attached to the screw S'. The heating current then flows through the frame F, and the tongue T. To diminish heating in the bearings of the tongue, a thin copper wire

[1] Made by the General Electric Company.

spiral, W, is inserted between the frame and the short end of the tongue. To reduce sparking at the silver studs, a small condenser is introduced between the block S′ and the frame F.

Evacuated tubes containing mercury, of the form shown in Fig. 12, are also used in connection with a relay for making and breakin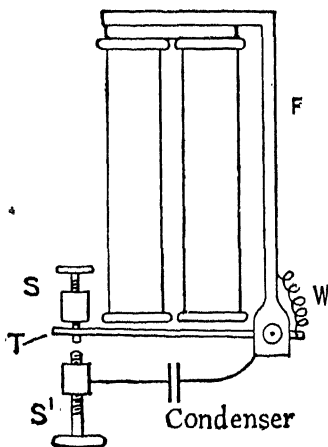g the heating circuit. When the tube is in the position shown, the current flows from the wire terminals A and B through the mercury in the tube. When current
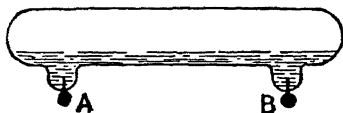
FIG. 12.

passes through the coils of the relay, the tube is tilted, the mercury flows to one end of the tube and electrical connection between A and B is broken.[1]

The use of a battery for actuating the relay can be avoided by tapping the main heating circuit. A diagram of a suitable arrangement for use with a 220-volt D.C. circuit is shown in Fig. 13.

Although the arrangement just described is satisfactory when a thermostat is in use only for short periods, it suffers from the disadvantage that, when in continuous use over a long period of time, the sparking which takes place at the mercury surface of the thermo-regulator brings about a serious fouling of the mercury by oxidation. This difficulty can be overcome by the use of a triode thermionic valve, the anode current from which is used to actuate an electromagnetic relay.[2] This current can be stopped practically completely by applying a negative potential to the grid and the current in the circuit broken at the mercury surface can be cut down to a few micro-amperes when the thermo-regulator is arranged to control the potential of the grid. The mercury surface therefore keeps clean during months of continuous use. Moreover, an adjustable steel needle, which is not wet by mercury, may be used in place of the platinum wire to make and break contact with the mercury.

[1] Another convenient form of tube has been described by P. T. Black, *Science*, 1934, **79**, 322.

[2] D. J. and J. J. Beaver, *J. Ind. Eng. Chem.*, 1923, **15**, 359; E. A. Cooke and J. C. Swallow, *J. Sci. Instr.*, 1929, **6**, 287.

The lag due to the adhesion of mercury to platinum is thus prevented.

The arrangement is shown diagrammatically in Fig. 14, and may be operated by direct current from the mains. The filament of the valve is connected in series with two equal resistances (*e.g.* carbon filament lamps) R_1 and R_2, chosen so as to give the correct current for heating the
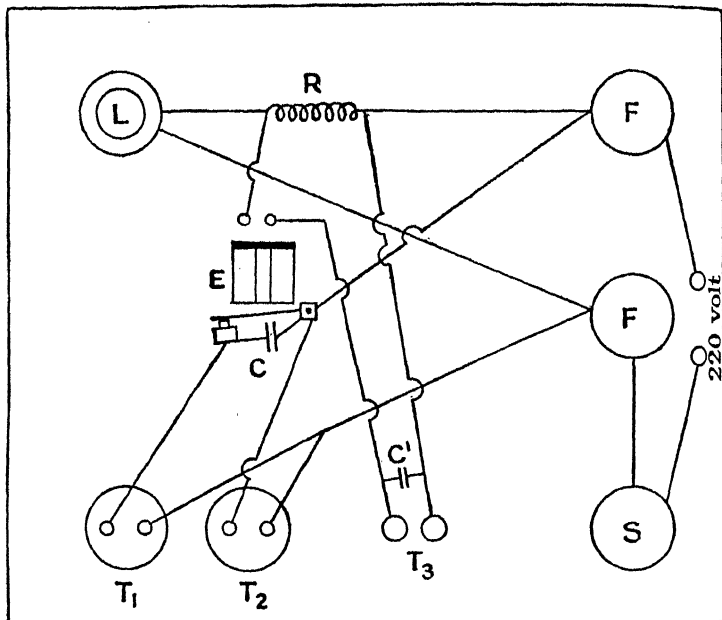
FIG. 13.

S=an electric light switch, F=fuse, R=9 inches of 34-gauge nichrome wire, L=8 c.p. carbon lamp, E=electro-magnetic relay (10 ohms), T_1=terminals for heating lamp (100 watts), T_2=terminals for motor, T_3=terminals for thermo-regulator, C=condenser (0·25 mf.), C′=condenser (0·1 mf.).

filament. The anode plate is connected with the positive terminal through the windings, P, of the electro-magnetic relay. The grid is connected to the negative terminal by a 5 megohm grid-leak, R_3, and to the filament through the thermo-regulator, T.

If the current from the mains is at 220 volts, the positive terminal will be at 110 volts positive potential relatively to

the filament, and the negative terminal will be at 110 volts
negative potential with respect to the filament. When
contact is made at the thermo-regulator, the grid will be at
the same potential as the filament, and current will flow to
the anode and thence through the windings of the relay,
thus breaking the heating circuit. When contact is broken
at the thermo-regulator, the grid becomes negative to the
filament and the anode current stops. The heating circuit
is then closed at the contact C. A resistance is placed across
the contacts to minimize sparking.

Thyratron relay.—When alternating electric current is
available, sparking at mercury or other surfaces can be
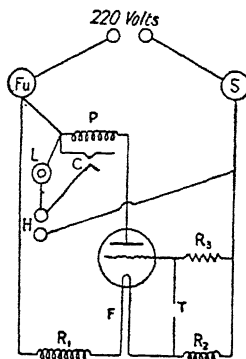
FIG. 14.

Fu = fuse, S = switch, $R_1 R_2 = 32$ c.p. carbon lamps, $R_3 = 5$ megohm
grid leak, F = filament of valve (Marconi P 625 A), P = post office relay
(1,000 ohms resistance), C = contacts at relay, L = 10 watt lamp,
H = terminals of heating circuit, T = thermo-regulator.

eliminated by replacing the electro-magnetic relay by a
thyratron (gas-filled tube) relay,[1] which differs from a
vacuum thermionic valve in that it can pass a relatively
very large current of electricity, the strength of which is
independent of the grid potential provided this has a mini-
mum positive value. A convenient arrangement [2] is shown
diagrammatically in Fig. 15.

The battery B is connected through the resistances R_1
(0·25 megohm) and R_2 (1 megohm) with the thermo-

[1] For example, the argon filled tube, GT₁C, of the General Electric Co.
[2] See Reilly and Rae, *Physico-Chemical Methods*, 3rd ed., I, 189 :
II, 429.

regulator T ; and the positive pole of the battery is also connected with the grid G, of the thyratron tube. The anode circuit, which includes a 0·5 amp. fuse, Fu, and the heating element, H, is supplied from the A.C. mains. Since a potential must not be applied to the anode until the thyratron cathode is fully heated, a switch, with a magnetic release, is inserted in the anode circuit and is not closed until the cathode is fully heated. For the heating of the cathode, the voltage of the mains is reduced by means of a transformer to the required value (2–4 volts).

When the bath is below the desired temperature, the thermo-regulator circuit is open and the battery makes the grid positive with respect to the cathode and full current flows through the thyratron and heater. When the temperature of the bath rises and contact is made at the thermo-regulator, the battery maintains the grid at a negative potential with respect to the cathode. Since alternating current is used, the plate A of the thyratron becomes alternatively positive and negative, and although, when A becomes negative the current through the thyratron stops, it starts again at the next half-cycle, provided the grid is positive, *i.e.* provided the circuit at the thermo-regulator is broken. When, however, the grid is made negative, then the current stops when A becomes negative and starts again only when the grid becomes positive, *i.e.* when the temperature of the bath falls and the thermo-regulator circuit is broken.
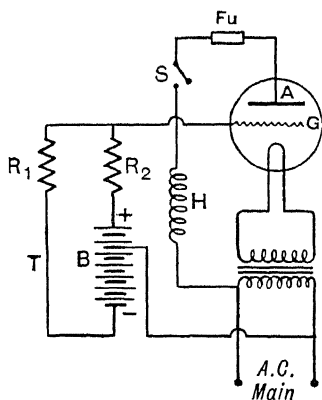
FIG. 15.

The strength of current which can be carried by the valve is limited (0·3–1·0 amp.), and the heater in the thyratron circuit should therefore be used only for keeping the temperature variations within small limits. The temperature of the bath should be maintained chiefly by a second heater which is constantly in action.

2. *Temperature below that of the surroundings.*—In the case of small thermostats, the maintenance of a constant bath

temperature lower than that of the surroundings can readily be effected by means of a regulated supply of cold water. In the case of the toluene-mercury regulator designed by Foote [1] (Fig. 16), a slow stream of ice-cold water flows in at h. When the temperature of the bath is below the desired temperature, the mercury in c falls and the end d of the tube f is opened. The cold water thus flows out through the tube f to the waste. As the temperature rises, the mercury
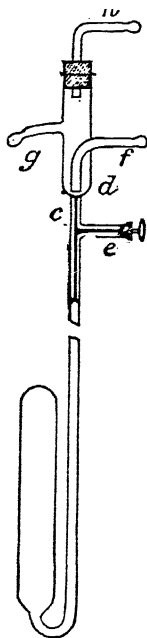
FIG. 16.
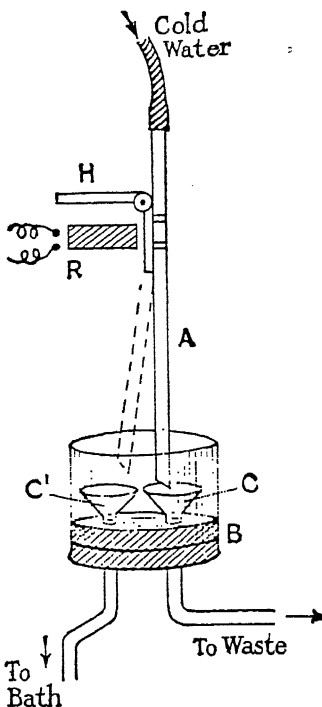
FIG. 17.

also rises and closes the opening d, and the ice-cold water now flows out through g to the bath. The amount of water flowing through h must not be too great, and must be regulated so that it can be carried away by the tube df when the latter is open. The constant-temperature bath must, of course, have an overflow pipe.

A thermo-regulator of the type shown in Fig. 9 or Fig. 10

[1] See also Bratton, *Science*, 1939, **89**, 589.

may also be used to regulate the flow of cold water to a constant-temperature bath.[1] The arrangement is shown in Fig. 17. The tube A through which the cold water flows, is fastened to an iron hinge, H, near which the electro-magnet R is fixed. So long as the temperature of the bath is below the temperature for which the thermo-regulator is adjusted, cold water flows into the cup C, and passes to waste ; but when the temperature of the bath rises and so brings about the closing of the electric circuit through the regulator, a current passes through the coil of the electro-magnet. The iron hinge is attracted by the electro-magnet, the tube A is pulled to the left, and the cold water then discharges into the cup C' and flows to the bath.

While the arrangements just described are satisfactory in the case of small thermostats, a combined cooling and heating arrangement is preferable, or necessary, with larger thermostats. The cooling of the bath liquid, which may be water, a solution of calcium chloride in water or a solution of ethylene glycol in water, depending on the temperature of the bath, is effected by circulating the cooling liquid through a coil or through tubes immersed in the bath liquid. To secure constancy of temperature the cooling effect of this arrangement is combined with a low-powered heating element immersed in the bath liquid and controlled by means of a suitable thermo-regulator. Depending on the bath temperature desired, the cooling liquid may be maintained at a suitable temperature either by means of ice or of the evaporator unit of a refrigerator.

The circulation of a cooling liquid can be avoided by fitting the cooling unit (evaporator) of a refrigerator, A, through a side of the constant temperature bath itself (Fig. 18), and for this purpose a small unit, such as electrolux short unit, type 100, is very suitable. By this means, bath temperatures below that of the surroundings, down to, say, $-10°$, can be obtained. Constancy of temperature is secured by combining the effect of the cooling unit with a controlled heating element.[2]

Circulation of Water.—The maintenance of a constant temperature in apparatus outside the thermostat (*e.g.* refractometer) is best effected by circulating water from the

[1] Brönsted and La Mer, *J. Amer. Chem. Soc.*, 1924, **46**, 555.
[2] Parks, *Ind. Eng. Chem.* (*Anal.*), 1933, **5**, 357 ; Benford and Ingold, *J. Chem. Soc.*, **1938**, 929.

thermostat through the apparatus by means of a pump, of which there are various forms on the market.

For most purposes it will be found that the Luther pump is very efficient and convenient to use. A diagram of this pump is shown in Fig. 19. Attached to the pulley *m*, is the rod *a*, which carries at its lower end the four hollow arms *b*, with which there also communicates the tube *d*. This series of tubes is enclosed within the metal box *f*, furnished with
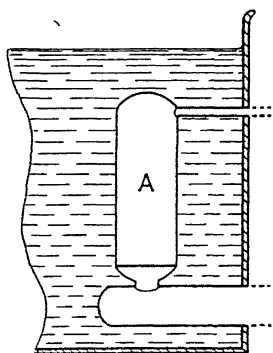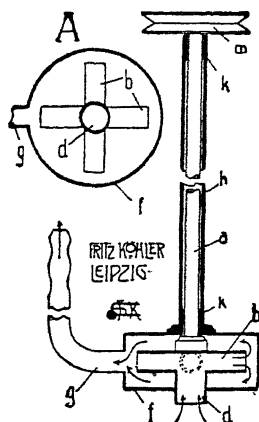
FIG. 18.   FIG. 19.

the outlet tube *g*. The axle rod, *a*, runs in the bearings *k* enclosed within the tube *h*.

When in use, the metal box *f* is entirely submerged. On causing the hollow cross to rotate rapidly (by means of an electric motor, for example), water is sucked in at *d* and forced out through *g*. By this means water from the thermostat can be caused to circulate through apparatus and be returned again to the thermostat.

CHAPTER IV

DENSITY OF GASES AND VAPOURS

DETERMINATIONS of the density of gases and vapours are of value for the chemist on account of the fact that from the value of the density the molecular weight of the substance in the gaseous condition at the temperature of vaporization can be calculated.

The absolute density of a gas is the mass of unit volume, *i.e.* of 1 litre (or of 1 ml.) ; but as the volume of a gas is greatly influenced by temperature and pressure, the density of a gas is defined as the mass of unit volume at the temperature of 0° and under the pressure of 760 mm. of mercury. Frequently, however, use is made of the relative density, *i.e.* the weight of a given volume of the gas compared with the weight of the same volume of another gas, when measured under the same conditions of temperature and pressure.

Since, in chemistry, determinations of the density of gases are chiefly made for the purpose of obtaining the molecular weight, and since oxygen is now taken as the basis of atomic weights, it is better also to take it as the basis of densities and of molecular weights. If the density of a gas is referred to that of oxygen equal to 32·00, the number expressing the density also expresses the molecular weight of the gas.

Determination of the Density of a Gas.—For the determination of the density of a gas, the most convenient and at the same time most accurate method is to weigh the gas in a glass globe of known volume.[1] The globe, which should be blown strong enough to withstand a pressure of 1 atm., may have a volume of 200–500 ml. ; and sealed into

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[1] For the precautions which must be adopted and the corrections to be applied in accurate determinations of the density of gases by direct weighing, see Rayleigh, *Proc. Roy. Soc.*, 1899, **55**, 340 ; Morley, *Amer. J. Sci.*, 1891, **41**, 220 ; *Z. physikal. Chem.*, 1896, **20**, 68 ; Scott, *Phil. Trans.*, 1893, A, **184**, 543 ; Travers, *Experimental Study of Gases* (Macmillan).

it is a glass tube furnished with a well-fitting glass tap (Fig. 20).[1] Before being used, the tap must be uniformly coated with a lubricant, the best being that recommended by Ramsay.[2] If it is desired to determine the absolute density of a gas, the volume of the globe must first be ascertained. This is done by weighing the globe empty and then filled with distilled water at a known temperature.

To fill the globe with water, it is first exhausted as completely as possible by means of a pump,[3] and the tap then opened while the end of the tube dips under the surface of a quantity of recently boiled distilled water. When the globe is full, it is placed, the tap being open, in a constant temperature bath. When the water has taken the temperature of the bath, the tap is closed, *so that its bore remains full of water*, and the tube above the tap is dried by means of filter paper. The globe full of water is then weighed to 1 cg. The difference between the weight of the exhausted globe and of the globe full of water gives the apparent weight in air of the water. To obtain the true weight of the water in the globe and, therefore, the internal volume of the globe, the correction for buoyancy (p. 19) must be applied; or the volume corresponding to the apparent weight may be calculated from the table on p. 21.
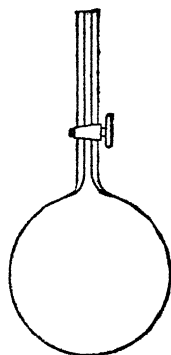
FIG. 20.

The water is then removed from the globe by means of a filter pump, and the globe dried by washing successively with alcohol and ether, warming in a steam oven and exhausting several times till all the ether has been removed.

After a sufficient time has elapsed to allow the globe to regain its normal volume,[4] it is exhausted by means of a Fleuss or Hyvac pump and weighed; it is then filled with the gas, the density of which is to be determined, and

[1] Chancel flasks are also very suitable for this purpose.

[2] This is made by melting together 3 parts of vaseline, 1 part of paraffin, and 6 parts of soft rubber.

[3] A Fleuss or Hyvac pump is the most convenient, but an ordinary water pump may also be used here.

[4] A glass vessel, after having been heated, does not immediately acquire its true volume on cooling; and an appreciable error may be introduced if sufficient time is not allowed to elapse.

again weighed. These weighings should be carried out as accurately as possible, and, in order to eliminate as far as possible errors due to the buoyancy of air, a similar globe of approximately the same weight and volume should be used in both cases be used as a counterpoise. Knowing the volume of the globe and the weight of the gas, knowing also the temperature and pressure at which the globe was filled, the density of the gas or the weight of 1 ml. at N.T.P. can be calculated.

If W is the weight of the gas filling the globe, the volume of which is v ml., and if $t°$ is the temperature and p mm. of mercury the pressure at which the globe was filled, then the volume of the gas at N.T.P. would be—

$$v_0 = \frac{v \times 273 \times p}{(273 + t) \times 760}$$

The absolute density of the gas is therefore $d = \dfrac{W}{v_0}$.

Since 1 g.-molecule of a gas at N.T.P. occupies approximately the volume of 22,400 ml. the approximate molecular weight [1] of the gas is given by $M = \dfrac{22,400 \times W}{v_0}$.

EXPERIMENT.—*Determine the Absolute Density of Dry Air.*
The volume of the globe and its weight when exhausted are first determined, as ex-

FIG. 21.

plained above. The dry globe is then clamped in a bath of water kept at a constant temperature, say 25°, so that the globe is entirely immersed, but not the stop-cock (Fig. 21); and a T-tube, a, is attached to it by means of pressure tubing. The side tube of a is connected with a Fleuss or Hyvac pump by means of pressure tubing [2] on which there is a screw-clip, I; and to the end of a a tube of calcium chloride is attached, also by means of pressure tubing furnished with a screw-clip, II. This clip is kept closed, and the globe exhausted by means
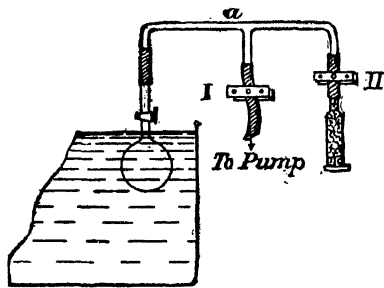
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[1] Avogadro's law holds accurately only at zero pressure.
[2] In place of the rubber tubes and clips I and II, a three-way tap may with advantage be inserted at a (Fig. 21).

of the pump ; then clip I is closed and II partially opened so that a *slow* current of air is drawn into the globe. The globe should in this way be twice exhausted and twice filled. It is now allowed to stand in open communication with the air for about five minutes so that the gas may take the temperature of the bath, and the stop-cock is then closed. The tube *a* is disconnected, and the globe removed from the bath and carefully dried. It is then allowed to take the temperature of the balance case and weighed, a similar globe being used as a counterpoise. The barometer must also be read and the necessary corrections made (see Appendix).

The absolute density is then obtained by means of the formula on p. 46. (Density of dry air at $0°$ c. and under a pressure of 760 mm. of mercury$=1·2928$ g. per litre.)

EXPERIMENT.—*Determine the Density of Carbon Dioxide relative to that of Air, and calculate the Molecular Weight of the Gas.*

First weigh the globe filled with dry air in the manner described in the previous experiment ; then fill it with carbon dioxide and weigh again.

For the purpose of filling the globe with carbon dioxide, an apparatus for generating this gas—best a Kipp apparatus —is attached to the calcium chloride tube, and after the globe has been exhausted, a *slow* current of gas is allowed to pass into it, the exhaustion and filling being carried out twice after all the air has been driven from the connecting tubes. The globe is then left in free communication with the CO_2 apparatus for about five minutes, the tap then closed, and the globe disconnected. Since the gas in the globe is under a pressure greater than atmospheric (owing to the pressure in the generator), it is necessary before removing the globe from the bath slowly to open and then immediately to close the glass stop-cock, so that the pressure in the globe becomes equal to the atmospheric pressure. The globe is then dried as before and weighed.

Since the globe was filled with air and carbon dioxide at the same temperature and under the same pressure, and since the volume of the two gases is equally affected by changes of temperature and pressure, the ratio of the weights determined above will give the relative density, *i.e.*—

$$\frac{\text{density of } CO_2}{\text{density of air}} = \frac{\text{weight of } CO_2}{\text{weight of air}}$$

The error in the determinations must not exceed 1 per cent. (Density of carbon dioxide at 0° C. and under a pressure of 760 mm. of mercury=1·9768 g. per litre.)

Further Experiments.—Determine the density of hydrogen and of oxygen; and also of a mixture of these two gases. From the density of the mixture, calculate its composition.

Degree of Dissociation of a Gas.—Since the molecular composition of a dissociating gas varies with the temperature, the degree of dissociation, and the dissociation constant at different temperatures, can be calculated from determinations of the density.

EXPERIMENT.—*Determine the Density of Nitrogen Tetroxide at Different Temperatures.*

In the hard glass test tube A (Fig. 22), place 8–10 grams
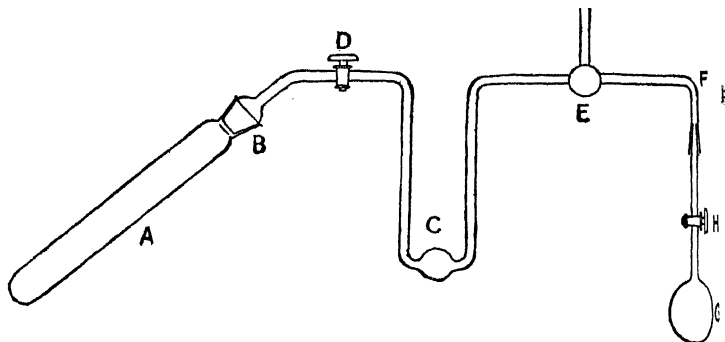
FIG. 22.

of roughly ground and well dried lead nitrate. Connect the U-tube C, by means of the ground joint B, and open the tap D. The ground joint and tap may be lubricated with phosphoric acid. Exhaust the apparatus through the three-way tap E, and gently heat the tubes so as to get rid of moisture. Place the U-tube in a freezing-mixture of ice and salt and heat the lead nitrate, the three-way tap E being open to the air. Nitrogen tetroxide will be evolved and will condense in the U-tube. When sufficient nitrogen tetroxide has collected, close the tap D and disconnect the tube A. The tube F is then connected by a ground joint with the globe G, which should have an internal volume of not less than about 400–500 ml. The weight of the empty globe and its volume should previously have been deter-

mined as in previous experiments, a globe of similar dimensions being used as a counterpoise. Exhaust the globe through the tap E, and, after removing the ∪-tube from the freezing-mixture, allow nitrogen tetroxide to pass into the globe. Exhaust and refill the globe with nitrogen tetroxide, and then place the globe in a freezing-mixture and collect 2–3 ml. of liquid nitrogen tetroxide in the globe. Close the tap H and the three-way tap E, and disconnect the globe G. This is then placed in a thermostat at a temperature of about 20°, the tap H being opened slightly so as to allow the excess of nitrogen tetroxide to escape, the escaping gas being passed through a tube of moist caustic potash. When all the liquid nitrogen tetroxide has evaporated, and gas ceases to escape from the globe, close the tap H, remove the globe from the thermostat, dry and weigh. The barometric pressure should also be ascertained.

The globe with nitrogen tetroxide should then be placed in a bath at, say, 40°, and when it has taken the temperature of the bath, the tap H is slowly opened, so as to equalize the pressure, and then closed. Dry and weigh as before. Carry out similar determinations at, say, 60°, 80° and 110°, using an oil bath.[1]

At each temperature calculate the density of the gas and the apparent molecular weight. It must be noted at the higher temperatures that the volume of the globe must be corrected for the expansion of the glass. If V is the volume of the globe at temperature t, the volume at temperature t' will be $V[1+0.000025(t'-t)]$, where 0.000025 is the coefficient of cubical expansion of glass.

Calculations.—As the temperature is raised, the N_2O_4 molecules dissociate into NO_2 molecules and at each temperature an equilibrium is established represented by $N_2O_4 \rightleftharpoons 2NO_2$. The degree of dissociation at a given temperature can be calculated by means of the expression $a=(d_t-d_0)/d_0$, where d_0 is the observed density and d_t is the density of the undissociated N_2O_4. Since the molecular weight is proportional to the density, $a=(M_t-M_0)/M_0$, where M_t is the molecular weight of N_2O_4 (92), and M_0 is the apparent molecular weight of the gas at the given temperature.

If the total pressure (1 atm.) of the equilibrium mixture is represented by P, the partial pressure of the N_2O_4 molecules will be given by $p_{N_2O_4}=\dfrac{1-a}{1+a} \cdot P$, and the partial pressure of the NO_2 molecules

[1] See Sainte-Claire Deville and Troost, *Compt. rend.*, 1867, **64**, 237; E. and L. Natanson, *Ann. Physik*, 1886, (iii), **27**, 606.

will be, $p_{NO_2} = \dfrac{2a}{1+a}$ P ; and the equilibrium constant K_p will be given by the expression

$$K_p = \left(\frac{2a}{1+a} \cdot P\right)^2 \Big/ \frac{1-a}{1+a} \cdot P = 4a^2P/(1-a^2).$$

From the determinations of the density at different temperatures the student should calculate the value of a and the value of K, and the values of log K_p should be plotted against $1/T$. From the curve so obtained, values of the equilibrium constant [1] can be read off, and by applying the van't Hoff isochore, in its integrated form

$$\log_{10}\frac{K_1}{K_2} = \frac{q_p}{2 \cdot 303 \times 1 \cdot 987}\left(\frac{T_2 - T_1}{T_1 T_2}\right)$$

the value of q_p, the heat evolved when the reaction takes place at constant pressure, can be calculated.
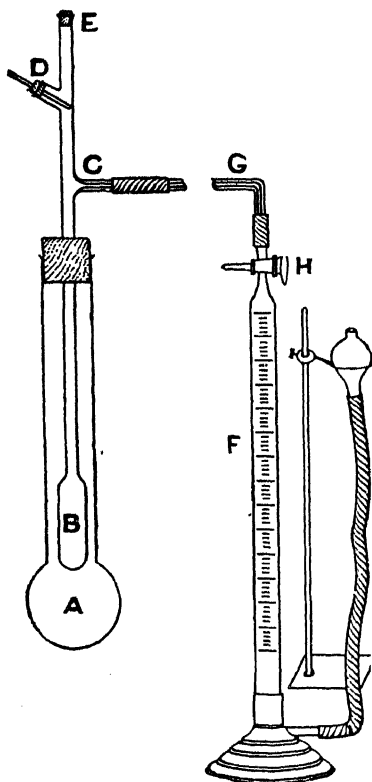
Determination of Vapour Density.—For the determination of the density of the vapour of a substance, when the latter is not a gas at the ordinary temperature, the method commonly employed is that due to Victor Meyer or the allied one due to Bleier and Kohn.

FIG. 23.

1. *Victor Meyer's Method.*—The Victor Meyer apparatus (Fig. 23) consists of a cylindrical vessel B, having a long narrow neck, to which are sealed two side tubes C and D. The side tube D is closed by a tightly fitting india-rubber stopper, through which a glass rod, with flattened end, passes air-tight. It should be lubricated with graphite. The side tube C is connected with a bent capillary tube G the horizontal portion of which may be made from 1 to 1½ feet long ; the free end of this tube is then attached to the

[1] Bodenstein, *Z. physikal. Chem.*, 1922, **100**, 68 ; Verhoek and Daniels *J. Amer. Chem. Soc.*, 1931, **53**, 1250.

top of a Hempel gas burette F, filled with water. In making these connections, thick-walled india-rubber tubing should be employed, and the ends of the two glass tubes should be brought up close together.

The tube B, the upper end of which is closed by a rubber stopper, is placed in the wider tube A,[1] which contains a liquid the boiling-point of which is at least 20°–30° above the boiling-point of the liquid to be vaporized.[2] The mouth of A is closed by a large cork with a deep groove cut in one side to allow for expansion of the air in the tube. In order to allow B to pass through, it will be necessary to cut the cork in two pieces. To prevent bumping, a few pieces of porous tile, or similar material, are placed in A, and the liquid is boiled, the three-way stop-cock H being meanwhile open to the air to allow the expanded gas to escape. After the liquid in A has been boiling for ten minutes with such vigour that its vapour rises to the top of the tube, it is ascertained whether the temperature in B has become constant, by turning the tap H so as to make connection between B and the burette. If the temperature has become constant, the level of the water in the burette will remain unchanged. When constant temperature has been attained, the tap H is again opened to the air, the stopper at the end of B removed, and a weighed quantity of the liquid to be vaporized, contained in a small stoppered weighing bottle, is dropped on the flat end of the glass rod passing through D. The rubber stopper is then replaced, communication between B and the burette made through H, and the bottle with the liquid allowed to drop to the bottom of B by rotating the glass rod. On reaching the bottom of the tube, the liquid is vaporized, and expels a volume of air equal to the volume of the vapour at the particular temperature. As the air passes over into the burette, the reservoir must be lowered so that the level of the water in the reservoir and burette remain about the same. This diminishes the danger of leakage. So soon as the volume of air in the burette becomes constant, the water levels are adjusted and the tap H is closed. The

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[1] Although it is an advantage that the outer jacket tube should be transparent, the liability of a glass tube to be broken makes it advisable to substitute for glass an outer jacket of copper. A simple outer jacket composed of a straight glass tube and a beaker is described by Henderson, *J. Amer. Chem. Soc.*, 1912, **34**, 553. When a heating liquid other than water is employed, it will be necessary to fit a condenser to the outer jacket.

[2] A list of suitable heating liquids is given in the Appendix.

burette is then detached from the rest of the apparatus, and when the temperature has become constant, the water levels are again adjusted and the volume of the expelled air is read off. At the same time the temperature is read from a thermometer hung up beside the burette, and the height of the barometer is also noted.

If a gas burette is not available, an ordinary burette, arranged as shown in Fig. 24, can be employed. The upper end of the burette is closed by a rubber stopper, through which passes a T-tube furnished with a stop-cock, a. This takes the place of the three-way tap H of the Hempel burette. To this the tube G from the vaporization bulb is attached. The place of the movable reservoir is taken by the tube A, about 1 cm. wide, which is attached to the lower end of the burette, and is furnished with a piece of rubber tubing and spring clip B. The burette is filled by pouring water into A, while the tap a is open, and the level is adjusted by means of the spring clip B. When the experiment is in progress, and as air is being expelled from the vaporization tube into the burette, the water must be allowed to run from A so that the level in the two tubes remains about the same. At the end of the experiment the levels are accurately adjusted, and the volume of air in the burette is read off.
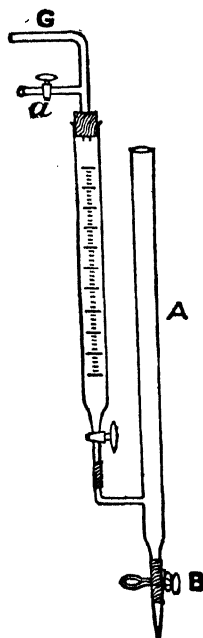
While the experiment is in progress, the gas burette should be protected from the heat of the flame and of the vapour mantle A, by means of a screen; or the burette may be enclosed in a jacket through which water circulates. The temperature is then determined by means of a thermometer hung inside the water-jacket.

FIG. 24.

Details.—It is desirable that the process of vaporization should take place as rapidly as possible; if it takes place slowly, diffusion and condensation of the vapour on the upper and colder parts of the tube may occur. The volume of air expelled will then be too small. For the same reason, the volume of air expelled should be read as soon as it becomes constant. In the case, further, of a substance

which dissociates in the vapour state, diffusion of the vapour through the air will lead to an increase in the degree of dissociation and, consequently, to the expulsion of a larger volume of air.

It is sometimes found that the stopper of the weighing bottle becomes fixed, so that the liquid is prevented from vaporizing, or vaporizes very slowly. To obviate this, the stopper should be loosened, or removed altogether (if the liquid is not too volatile), before the weighing bottle is dropped on to the glass rod at D. In this case, care must be taken that the weighing bottle is not filled so full that the liquid wets the stopper ; and the bottle must be lowered carefully, but as rapidly as possible, on to the glass rod by sliding it down the side of B with a strip of paper folded lengthwise into the shape of a V. To prevent vaporization as far as possible while the weighing bottle and liquid rest on the rod at D, the upper end of the tube B should be protected from the heat of the flame and the bath A, by means of a sheet of asbestos board, placed on the top of the cork closing the mouth of A.

To prevent the bottom of the tube B being broken by the fall of the weighing bottle, a small quantity of mercury should be poured into B before commencing the experiment, provided the temperature employed is not much above 150°. When high temperatures are used, a small pad of asbestos fibre can be used instead of the mercury.

After each experiment, all vapour must be removed from the tube by suction through a long glass tube which passes to the bottom of the vaporization tube.

The error in the determination of the density by the above method should not exceed 5 per cent.

EXPERIMENT.—*Determine the Density and Molecular Weight of Acetone or of Chloroform Vapour.*

The experiment is carried out as described above, water being used as heating liquid.

Calculation.—Let v be the volume of the air expelled, measured in ml. ; t the temperature of the air ; b the barometric pressure ; f the vapour pressure of water at the temperature t (*vide infra*) ; W the weight in grams of the substance taken. Then the volume of dry air expelled reduced to N.T.P. will be [1]—

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[1] In reducing the volume of air expelled to the volume of dry air at N.T.P., the vapour pressure of water, f, should be deducted from the barometric height, b, only when the vaporization tube was filled initially with dry air. If the air initially filling the vaporization tube was saturated

$$v_0 = \frac{v \times 273 \times (b-f)}{(t+273) \times 760}$$

v_0 is therefore equal to the volume which W g. of the vapour would have at N.T.P., and the weight of 1 ml. of the vapour would therefore be $\frac{W}{v_0}$. If the density is referred to that of an imaginary gas having a density equal to $\frac{1}{32}$ that of oxygen (1 ml. $= 0.00004465$ g.), one obtains—

$$d = \frac{W}{4.465 \times 10^{-5} \times v_0} = 22400 \frac{W}{v_0}.$$

This number also represents the molecular weight of the vapour, referred to the atomic weight of oxygen $= 16$.

The molecular weight may also be calculated more directly by means of the general gas equation. From $pv = nRT = \frac{W}{M} \cdot RT$, it follows that $M = \frac{W \cdot R \cdot T}{p \cdot v}$, where T is the temperature (absolute) of the expelled air. If the volume is expressed in ml. and the pressure in atmospheres, $R = 82.1$ and $p = \left(\frac{b-f}{760}\right)$.

with moisture, the vapour pressure of water, f, should not be subtracted from the barometric height, b. If the humidity of the air was h per cent, then only $(100-h)$ per cent. of the vapour pressure of water should be deducted; that is, in place of the term $(b-f)$ in the expression given above one should write $b - \frac{100-h}{100} \cdot f$, where h is the percentage humidity of the air (air of room) with which the vaporization tube was initially filled. Although the error introduced by using the expression given in the text will not, as a rule, exceed 1 or 2 per cent., the more exact expression should be employed in all accurate determinations of the vapour density by the Victor Meyer method (see Evans, *J. Amer. Chem. Soc.*, 1913, **35**, 958).

[1] It should be borne in mind that vapours do not behave in accordance with the laws of perfect gases, and the application of these laws, as in the calculation given above, cannot lead to correct molecular weights from vapour density measurements. Although, in the case of ordinary molecular weight determinations the deviations are of no practical importance, it should be borne in mind that when accurate values of the vapour density are desired, account must be taken of these deviations. This can be done by substituting for the ordinary gas law expression, Berthelot's form of the van der Waals equation of state. This equation takes the form (MacInnes and Kreiling, *J. Amer. Chem. Soc.*, 1917, **39**, 2350)—

where M is the true molecular weight, m is the mass of the substance, R is the gas constant, P and P_c are the corrected barometric pressure and the critical pressure respectively; T, T' and T_c are, in turn, the temperature at which the substance is vaporized, the temperature at which the volume of air is measured, and the critical temperature on the absolute scale. V' is the volume of the displaced air (see also, Kendall, *J. Amer. Chem. Soc.*, 1920, **42**, 2477; *Chem. News*, 1921, **122**, 31).

The value of the vapour pressure of water at different temperatures is given in the following table :—

VAPOUR PRESSURE OF WATER IN MILLIMETRES OF MERCURY

$t°$	p	$t°$	p	$t°$	p
0	4·6	11	9·9	21	18·6
1	4·9	12	10·5	22	19·8
2	5·3	13	11·2	23	21·0
3	5·7	14	12·0	24	22·3
4	6·1	15	12·8	25	23·7
5	6·6	16	13·6	26	25·2
6	7·0	17	14·5	27	26·7
7	7·5	18	15·5	28	28·3
8	8·1	19	16·5	29	30·0
9	8·6	20	17·5	30	31·7
10	9·2				

Two modifications of the Victor Meyer apparatus are worthy of mention. In the modification due to Weiser [1] (Fig. 25), the apparatus is more compact and easy to handle, and the whole of the vaporization tube, stem (B) as well as bulb (A), is surrounded by the vapour jacket, and so kept throughout at constant temperature. The substance to be vaporized is introduced through the neck C of the vaporization tube, which is then closed by means of a rubber stopper.

FIG. 25.

The MacInnes and Kreiling apparatus,[2] Fig. 26A, is also very compact, the vaporization tube, A, being only about 25 cm. long. Down the centre of this tube there passes tube B, with a bore of about 1·5 cm. The device used for introducing the liquid to be vaporized, consists of a brass rod, R (Fig. 26B), near the lower end of which a notch has been filed. This brass rod fits smoothly into a glass tube, G, which passes through a rubber stopper closing the upper end of the tube B ; and a gas-tight connection between the
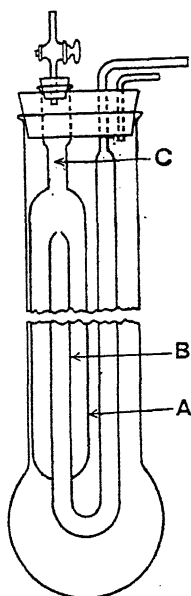
[1] J. Physical Chem., 1916, **20**, 532.
[2] J. Amer. Chem. Soc., 1917, **39**, 2350.

upper end of the glass tube and the brass rod is made by
means of a piece of rubber tubing. The liquid to be
vaporized is contained in a small glass bulb, C, with a
narrow, thin-walled glass neck bent into the form of an U.
This narrow tube is fitted into the notch on the brass rod,
in the position shown in Fig. 26B, and the bulb is kept in
position by means of a rubber band. The glass tube and
brass rod are passed through the stopper in B to such a
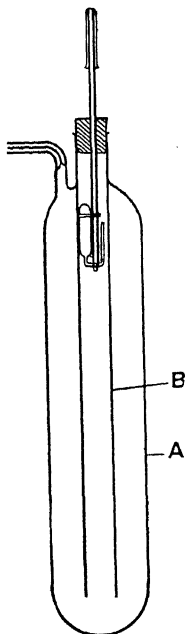
FIG. 26A.
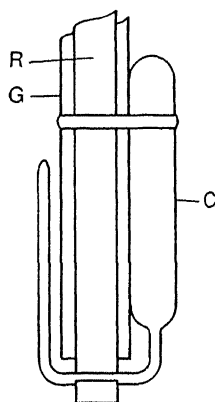
FIG. 26B.

distance that the bulb with liquid is in the upper portion of
tube B (Fig. 26A).

In use, the vaporization tube is supported by means of a
cork or rubber ring in a wider glass (pyrex) tube to serve
as a vapour jacket. The temperature of the heating vapour
should be about 50° higher than the boiling point of the
liquid under investigation. When the temperature of the
vaporization tube has become constant, the capillary is
broken by pulling at the upper end of the brass rod, so as
to break the neck of the bulb against the lower end of the

glass tube G.   Vaporization of the liquid takes place and
air is expelled.

   2. *Bleier and Kohn's Method.*—In Victor Meyer's method,
as we have seen, the pressure is maintained constant (equal
to that of the atmosphere), and the increase in volume due
to the formation of vapour is determined.   In Bleier and
Kohn's method, however, the volume is maintained constant,
and the increase in pressure measured.[1]   (Before using this
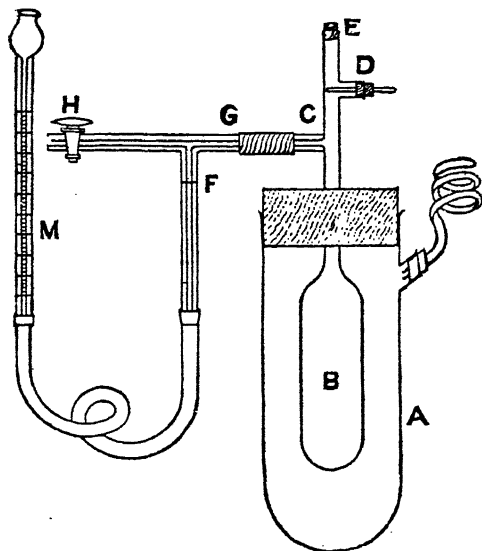
FIG. 27.

method, read through the description of the Victor Meyer
apparatus and method.)

   The apparatus, as modified by Lumsden,[2] is shown in
Fig. 27.   The vaporization tube B is essentially the same as
in the Victor Meyer apparatus, only much shorter.   It is
fitted into the wide boiling-tube A, which carries a spiral
glass condenser, by means of an india-rubber bung.[3]

[1] Bleier and Kohn, *Monatsh.*, 1899, **20**, 505.
[2] Lumsden, *J. Chem. Soc.*, 1903, **83**, 342.
[3] In the original apparatus described by Lumsden, the boiling-tube was
sealed to the neck of the vaporization tube.   This has the advantage that
heating liquids which attack rubber can be used.   It has, however, the
disadvantage that the apparatus is thereby rendered considerably more
expensive, and if the outer boiling-tube is broken, repair is impossible.   It

The apparatus is best supported on a square asbestos heating box, and while the liquid in A is being boiled (use porous tile to avoid bumping), the stop-cock H is kept open to the air. To protect the upper part of the tube B from the hot air, a sheet of asbestos board, cut with a hole for the passage of the tube, is placed on the top of the rubber bung.

The perpendicular capillary tube F, on which there is a fixed mark, is connected by means of thick-walled rubber tubing with the tube M, which is graduated in millimetres. The ends of the rubber tube must be wired to both F and M. This tube must be filled with so much mercury that when the mercury in F is at the fixed mark, the meniscus in M is at the top of the graduated portion, or even a little above it. Care must be taken that the mercury forms a continuous thread unbroken by air-bubbles.

The preliminary heating of the vaporization tube is carried out as with the Victor Meyer apparatus. The attainment of constant temperature is shown by the mercury in tube F remaining stationary when the stop-cock H is closed.

When constant temperature has been attained, introduce the weighing bottle with substance as with the Victor Meyer apparatus, and replace the stopper at E. Adjust the mercury so that it stands at the fixed mark on F, close the stop-cock H, and then allow the weighing bottle to fall to the bottom of B, which must be protected by mercury or asbestos.

As the liquid vaporizes in B, the pressure in the apparatus will increase. The mercury should always be kept near to the mark on F by raising the tube M. When the vaporization is complete and the mercury has become stationary, place the manometer tube M close to the tube F, and adjust the level so that the mercury stands at the mark on F. Then read off the difference in height (p) of the two mercury surfaces. This represents the increase of pressure due to the vapour produced.

With the apparatus of Bleier and Kohn or Lumsden,

is much better, therefore, in all cases in which the heating liquid permits of a rubber bung being used, to adopt the apparatus as shown in Fig. 27.

In Lumsden's original apparatus, also, the horizontal capillary CG consisted of one piece. As this is very liable to be broken, it is better to cut the capillary, and connect the two pieces by means of thick-walled rubber tubing. In doing this, the two ends of glass tube should be brought up close to each other, and the rubber tubing should also be wired on.

determinations of the vapour density are best carried out by a comparison method, as follows :—

First determine the increase of pressure (difference of level of the two mercury surfaces) produced by a known weight of a substance, the molecular weight of which is also known. From this calculate, by simple proportion, the difference of level which would be produced by 1 gram-molecule of the substance. Then determine the pressure produced at the same temperature by a known weight of the substance, the density of which is desired, and calculate from this how many grams of it would be required to give a pressure equal to that produced by 1 gram-molecule of the known substance. The number thus obtained represents the molecular weight of the substance, and also the density referred to that of oxygen equal to 32 (p. 54).

After each experiment, all vapour must be removed by a current of air.

Analysis of Binary Mixtures.—A useful application of vapour density determinations is to the analysis of binary mixtures of (normal) liquids, the vapour density of which is known. We have $\dfrac{W}{d} = \dfrac{w_1}{d_1} + \dfrac{w_2}{d_2}$, where w_1 and w_2 are the weights of the two liquids contained in W grams of the mixture, and d, d_1, and d_2 are the vapour densities of the mixture and of the single components. Hence

$$\frac{w_1 d_2 + w_2 d_1}{d_1 d_2} = \frac{W}{d}$$

From this, knowing the values of d_1 and d_2, W and d (determined experimentally), and remembering that $w_1 + w_2 = W$, the values of w_1 and w_2 can be calculated.

EXPERIMENT.—*Determine the Solubility of Carbon Disulphide in Methyl Alcohol at 25°.*

A mixture of pure carbon disulphide and methyl alcohol, contained in a stoppered bottle, is placed in a thermostat at 25° for 15–20 minutes, and is shaken at frequent intervals. It is then allowed to stand at rest till separation of the mixture into two layers has taken place. A portion of the upper layer is then pipetted off, a small quantity weighed in a small weighing bottle, and the vapour density then determined. The relative amounts of the two components is then calculated as above. (Compare Rothmund, *Zeitschr. physikal. Chem.*, 1898, **26,** 475.)

CHAPTER V

DENSITY AND VAPOUR PRESSURE OF LIQUIDS

A.—DENSITY OF LIQUIDS

THE density or specific gravity of a liquid is the mass of unit volume of the liquid, the unit of volume being the cubic centimetre (cm.³) or the millilitre (ml.). The latter unit is now generally adopted. Since, by definition, the millilitre is the volume occupied by 1 gram of water at the temperature of maximum density (4°), the density of water at this temperature, in g./ml., is unity; and the density at any other temperature is expressed relatively to that of water at 4° as standard and represented by $d_{4^\circ}^{t^\circ}$ (weighings are supposed to be corrected for the buoyancy of the air).

The *relative density* is the ratio of the weight of a given volume of the substance to the weight of an equal volume of water at the same temperature $\left(d_{t^\circ}^{t^\circ}\right)$; and the density of the substance at temperature t° is equal to the relative density multiplied by the density of water at that temperature.

Where sufficient liquid is available, the specific gravity can be determined, approximately, by means of hydrometers, or, more accurately, by means of the Westphal balance (Fig. 28), the use of which depends on the principle of Archimedes. The beam of the balance is graduated into ten equal parts, and four weights, in the form of "riders," are provided. The masses of these are in the ratios 1 : 0·1 : 0·01 : 0·001. In carrying out a determination of the density the balance is first adjusted for pure water. The glass sinker, which encloses a thermometer, is suspended in pure water from the end of the balance beam, and the unit rider is placed on the mark 10, or hung on the hook at the end of the beam, if only 9 divisions are shown on the beam. By means of a threaded counterpoise on the end of the beam,

or by means of a levelling screw in the base of the balance, the latter is adjusted till the two pointers are opposite each other.   The depth to which the sinker is submerged below the surface of the liquid and the temperature (say $t°$) should be noted.

The sinker is then dried and suspended in the liquid, the density of which is to be determined, the depth of submersion of the sinker being approximately the same as before.   The temperature of the liquid should also be the same as that of the water previously used.   If the density is less than unity, the unit rider, which was placed at the end of the beam in the case of water, must be moved to another
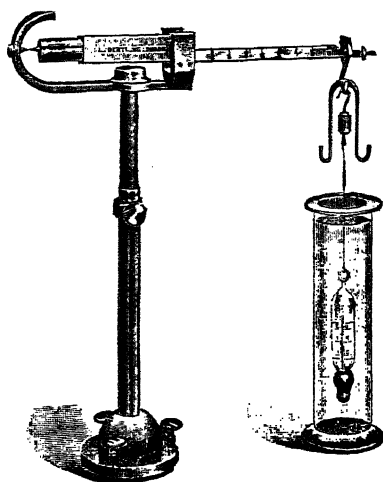
FIG. 28.

mark on the beam, and other riders must be placed at appropriate points so as to secure equipoise.   If, in order to obtain equilibrium, the unit rider must be placed on mark 8, the 0·1 rider on mark 7, the 0·01 rider on mark 9, and the 0·001 rider on mark 3, the specific gravity of the liquid is 0·8793.   (The riders are bent so as to form hooks on which other riders may be placed.   In this way more than one rider may be placed at the same mark on the beam.)   The value thus obtained represents the relative density, $d_{t°}^{t°}$, of the liquid.

If the density of the liquid is greater than unity, one of

the unit riders is placed at the mark 10 and the other unit rider and the smaller riders at appropriate points on the beam.

When only smaller quantities of liquid are available, or where greater accuracy is required, the density of liquids is best determined by means of vessels of accurately defined volume, called *pyknometers*. These are made of very varying shapes, but the simplest and most generally useful form is the Ostwald modification of the Sprengel pykno-meter (Fig. 29). The volume of the pyknometer should be about 5–15 ml. This will allow of an accuracy of about 1 unit in the fourth place of decimals, which will be quite sufficient for general purposes.
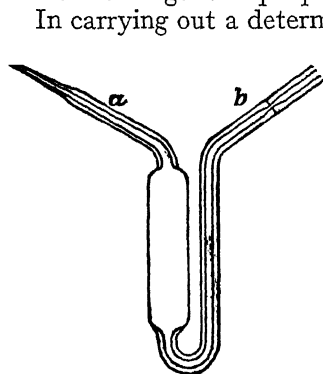
In carrying out a determination of the density of a liquid, the pyknometer must first of all be cleaned and dried, by wash-ing well with distilled water (if necessary, with other solvents first, and then with water), and then, successively, with a small quantity of alcohol (redistilled methylated spirit) and of ether. A current of clean air is then drawn through the tube.

FIG. 29.

The pyknometer, cleaned and dried, is first weighed empty. For this purpose it is sus-pended from the end of the balance beam by means of a double hook (Fig. 30), made either from platinum or from copper wire, preferably the former.[1] The pyknometer is then filled with distilled water, which has been recently boiled and allowed to cool, by attaching a piece of rubber tubing to the end *b*, and sucking gently while the end *a* dips in the water. The introduction of air-bubbles must be carefully avoided. The pyknometer thus filled is then suspended in a large beaker of water, the temperature of which must be kept constant to within 0·1°, as shown by a thermometer immersed in the water. Where a number of determinations of the density have to be made, it is more convenient to use a constant tem-

[1] It is not advisable to attach a wire permanently to the pyknometer, because of the greater difficulty in removing all moisture after the pykno-meter has been immersed in water.

perature bath (thermostat), the temperature of which is maintained constant by means of an automatic thermo-regulator (see p. 31).

The pyknometer may be suspended in the bath by means of a wire hook placed over a glass rod laid across the top of the beaker ; but it is better to use a holder cut from sheet zinc or copper (Fig. 31), and furnished with lugs which can be hooked over the edge of the bath. In the sheet of metal a hole is cut, which allows the body of the pyknometer to pass through, while the arms rest against the ends a and b. The length of the opening should be such as to allow the pykno-meter to pass so far through, that the mark on the tube b of the pyknometer is just above the metal plate ; and the water in the bath should be of such a height that it just touches the under side of the plate. By means of this arrangement, the danger of water getting into the ends of
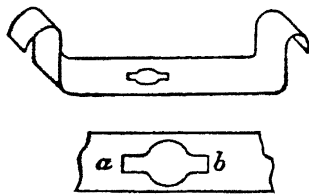
FIG. 30.   FIG. 31.

the pyknometer tubes is avoided, and the pyknometer is held in position more securely than by hooks.

When the pyknometer and its contents have taken the temperature of the bath (say after 15–20 minutes), the amount of water must be adjusted so that it fills the pykno-meter from the point of the tube a to the mark on b (Fig. 29). If there is too little water, a rod or tube carrying a drop of water is placed against the end of the tube a, when water will be drawn into the pyknometer by capillarity. If there is too much water, a piece of filter paper is carefully placed against the end of a, whereby water can be drawn from the pyknometer until the meniscus stands opposite the mark on b. This requires a little care. If too much water is with-drawn, more must be introduced as described above, and the adjustment again made by means of filter paper.

Instead of using filter paper, the adjustment can also be made in the following manner : A piece of rubber tubing, a

few centimetres in length, is placed over the end of b, and a rough adjustment made by pushing a glass rod into the open end of the rubber tube. The exact adjustment is then made by compressing the rubber tube with the fingers until the water is driven along to the mark. Before releasing the tube, any drop of water which may have collected at the point of a is removed by means of a glass rod. The pykno-meter is now removed from the bath, and the outside care-fully dried by means of a cloth, whereby care must be taken that none of the water is expelled from the pyknometer by the heat of the hand or by the natural expansion of the liquid when the density is being determined at temperatures below that of the room.[1] When the pyknometer has taken the temperature of the balance case, it is weighed.

If concordant and accurate weighings are to be obtained, it is essential that the outside of the pyknometer shall always be dried and treated in exactly the same way, since otherwise the amount of moisture which remains adsorbed on the surface will vary, and may cause an appreciable error.

After having determined the weight of the pyknometer filled with water, the pyknometer is once more dried out and filled with the liquid the density of which is to be determined. It is placed as before in the bath at constant temperature, the liquid is adjusted to the mark, the pyknometer dried with a cloth in the same manner as before, and weighed.

Calculation of the Density.—If the temperature at which the pyknometer is filled with water and with the other liquid is the same, then the ratio of the weight of liquid (W') to the weight of the water (W) gives the approximate density (uncorrected for the buoyancy of the air) of the liquid com-pared with that of water at the same temperature. This is represented by $d_t^t = \dfrac{W'}{W}$. For certain purposes, as in the determination of the relative viscosity (Chap. VI), this ratio is all that is required ; but in all cases where the specific gravity of the liquid is desired, we must compare the weight of the liquid at the temperature $t°$ with the weight of the same volume of water at $4°$. The density of the liquid at temperature $t°$ compared with water at $4°$ is then given by

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[1] This danger is avoided to a very great extent if a small bulb is blown on the arm of the pyknometer to the right of the mark b (Fig. 29).

the expression $d_{4°}^{t°} = \dfrac{W'}{W} \times D$, where D is the density of water

at $t°$. (See Table on p. 66.)

The value of the density just given must still be corrected for the buoyancy of the air by taking into account the density of the latter, and one therefore obtains as the expression [1] for the specific gravity of a liquid—

$$d_{4°}^{t°} = \frac{W'D}{W} - \frac{0·0012(W'-W)}{W}$$

If the temperature at which the pyknometer is filled with water and with the other liquid is not the same, a further correction is necessary for the expansion of the glass, and one obtains as the general expression for the specific gravity of a liquid—

$$d_{4°}^{t°} = \frac{W'D}{W} - \frac{0·0012(W'-W)}{W} + \frac{W'D}{W} \times 0·000024(t-t')$$

In this expression—

W is the apparent weight of water in air at temperature t ; W' is the apparent weight of the liquid in air at temperature t' ; D is the density of water at the temperature t ; $0·000024$ is the coefficient of cubical expansion of glass ; $0·0012$ is the mean density of air.

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[1] The use of either of the two formulæ given here for the calculation of the density may introduce considerable errors in the fifth decimal place of the density value, owing to variations in the value of the density of the air.   In the following table are given the values of the density of air half saturated with moisture, at different barometric pressures (corrected) :—

Temper- ature.	Pressure in millimetres.				
	740	750	760	770	780
10°	0·001211	0·001228	0·001244	0·001261	0·001278
15°	1190	1206	1222	1238	1254
20°	1168	1184	1199	1215	1230
25°	1146	1162	1177	1193	1208

For a discussion of various formulæ for correcting for the buoyancy of the air, see Wade and Merriman, *J. Chem. Soc.*, 1909, **95**, 2174 ; Block, *Z. angew. Chem.*, 1920, **33**, 198 ; Archibald and Ure, *J. Chem. Soc.*, 1924, **125**, 728 ; Barr, *ibid.*, p. 1040.

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DENSITY OF WATER AT DIFFERENT TEMPERATURES.

Temperature.	Density.	Difference in density for 0·1°, in units of the fifth decimal place.
0°	0·999874	
4°	1·000000	
5°	0·999992	0·8
6°	0·999969	2·3
7°	0·999931	3·8
8°	0·999878	5·3
9°	0·999812	6·6
10°	0·999731	8·1
11°	0·999637	9·4
12°	0·999530	10·7
13°	0·999410	12·0
14°	0·999277	13·3
15°	0·999132	14·5
16°	0·998976	15·6
17°	0·998808	16·8
18°	0·998628	18·0
19°	0·998437	19·1
20°	0·998235	20·2
21°	0·998023	21·2
22°	0·997800	22·3
23°	0·997568	23·2
24°	0·997326	24·2
25°	0·997073	25·3
26°	0·996811	26·2
27°	0·996540	27·1
28°	0·996260	28·0
29°	0·995971	29·0
30°	0·995674	29·7

B.—VAPOUR PRESSURE OF LIQUIDS

Although the molecules of a liquid, as a whole, are unable to overcome the force of cohesion, yet some, having a higher velocity than the average, are able to tear themselves away from the general mass and escape into space, where they move about freely as the molecules of a gas (or vapour). The liquid evaporates.

If, however, a liquid is placed in a closed vessel so that the escaping molecules cannot pass away into space, a pressure is produced. This pressure does not go on increasing indefinitely, but at each temperature attains a certain maximum value for a given liquid. At this point, as many molecules pass back into the liquid as escape from the liquid, and there exists, therefore, a dynamic *equilibrium*. This

equilibrium pressure is known as the *vapour pressure* of the liquid at the given temperature. As the temperature is raised, the vapour pressure increases, and when the vapour pressure becomes equal to the external pressure, or pressure on the liquid, the liquid *boils*.

The vapour pressure curve of a liquid is represented by the equation $\log p = A - \dfrac{B}{T}$, where A and B are constants for the given liquid. When, therefore, the logarithms of the vapour pressures are plotted against the reciprocals of the absolute temperatures, a straight line is obtained.

The ratio of the change of vapour pressure with the temperature is closely related to the latent heat of vaporization of the liquid ; and if the former is determined, the latter can be calculated. The relationship in question is expressed by the Clausius-Clapeyron equation, $\dfrac{d \log_e p}{dT} = \dfrac{L}{RT^2}$, where L is the latent heat per gram-molecule at the temperature T, R is the gas constant in heat units (1·987 cal.), and T is the absolute temperature at which the vapour pressure is equal to p. If it be assumed that over a small range of temperature, $T_2 - T_1$, the latent heat of vaporization remains constant, the Clausius-Clapeyron equation, on integration, yields the expression, $\log_e \dfrac{p_2}{p_1} = \dfrac{L(T_2 - T_1)}{R(T_2 \times T_1)}$, or, using decadic logarithms,

$$L = 2\cdot303 \times 1\cdot987 \times \frac{T_1 \times T_2}{(T_2 - T_1)} \cdot \log_{10} \frac{p_2}{p_1}$$

L is here the mean molar heat of vaporization over the temperature range $T_2 - T_1$. By dividing L by the molecular weight of the liquid, the latent heat of vaporization per gram is obtained.

I. Determination of the Vapour Pressure by the Ramsay-Young Method.—In determining the vapour pressure by the Ramsay and Young method,[1] a constant pressure is maintained and the temperature at which the liquid boils under that pressure is ascertained. The apparatus is shown diagrammatically in Fig. 32. The bulb of the thermometer T, which passes through a rubber bung, is covered with

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[1] *Phil. Trans.*, 1884, **175**, 37 ; *J. Chem. Soc.*, 1885, **47**, 42.

cotton wool,[1] and the lower end of the dropping-funnel C is drawn out to a point and bent so that it just touches the cotton wool. The thermometer and dropping funnel are placed, as shown, in a boiling-tube A, which is supported in a bath of water, glycerine, or oil, B, according to the temperature required. E is a tube to condense vapour and is placed in ice and water or in a freezing mixture. F is a large bottle which acts as a reservoir and serves to maintain a steady pressure. It is advisable to insulate the bottle F by packing it in a box with animal wool, or by surrounding it with thick felt.

The apparatus is first fitted together as indicated in
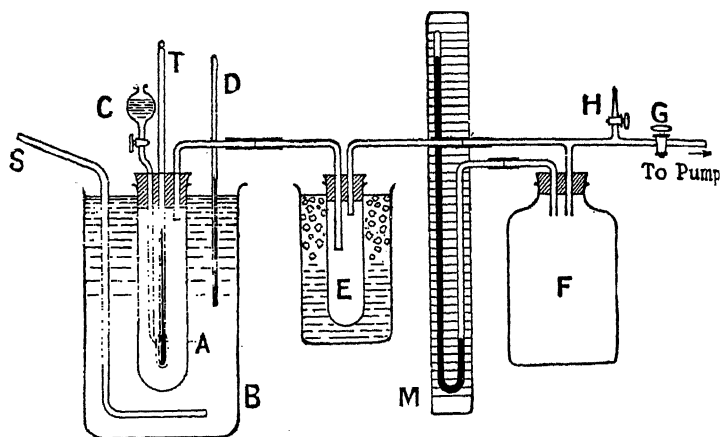
.FIG. 32.

Fig. 32, connections between the glass tubes being made by means of rubber pressure tubing. The ends of the glass tubes should be brought close together. Rubber bungs, also, must be used in closing the tubes and bottle. To ascertain if all connections are air-tight, the tap G is turned so as to make connection with an exhaust pump, and the apparatus exhausted. The tap G is then closed. If there is no movement of the mercury in the manometer M, the apparatus is free from leaks, and the determinations of the vapour pressure may begin.

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[1] The cotton wool is teased out into a thin layer and then wound round the bulb of the thermometer. Avoid using too thick a layer of cotton wool.

EXPERIMENT.—*Determine the Vapour Pressure of Benzene at Different Temperatures.*

A quantity of purified benzene is placed in the funnel C, and the pressure within the apparatus reduced by means of an exhaust pump to about 30 mm. The temperature of the bath A, as shown by the thermometer D, should not be higher than 12°–15°, and the water should be kept stirred by means of the stirrer S. A few drops of benzene are now allowed to flow from the funnel so as thoroughly to moisten the cotton wool surrounding the bulb of the thermometer T. As evaporation takes place, more benzene must be allowed to flow from the funnel so that the cotton wool is always thoroughly moistened with liquid. As the benzene evaporates, the temperature recorded by the thermometer T will alter and reach a steady value, so long as the pressure in the apparatus is kept constant. The experiment is continued until this steady temperature is reached. This temperature is the boiling-point of benzene under the pressure within the apparatus; or, in other words, the pressure shown by the manometer represents the vapour pressure of benzene at the temperature recorded by the thermometer T. Temperature and pressure are carefully read. The correction for change of volume of the thermometer bulb by reduction of pressure, which may amount to 0·1°–0·2° at the lowest pressure, may be neglected.

The thermometer T should be chosen with a range such that the mercury thread lies entirely within the tube A. If this cannot be done, and if the mercury thread rises above the rubber stopper, a correction for the exposed stem must be introduced. (See Appendix.) The temperature of the bath B should be regulated so that it is not more than 10°–12° above that shown by the thermometer T.

Having recorded, as above, the boiling temperature and corresponding pressure, air is admitted through the tap G until a pressure of about 60 mm. is obtained, and the boiling-point of benzene under this pressure determined. The temperature of the bath B is raised and kept at 10°–12° above that shown by the thermometer T. Make a series of determinations at different pressures up to 760 mm., the increments of pressure being increased as the temperature is raised.

Determinations of the vapour pressure of other liquids,

e.g. water, carbon tetrachloride, chlorobenzene, acetone, ethyl alcohol, should also be carried out.

Calculations.—In the case of each liquid investigated, draw a large-scale graph of the vapour pressure against temperature. Plot also the logarithms of the vapour pressure against the reciprocals of the absolute temperatures. Compare the graphs with those obtained by plotting the known values of the vapour pressures.

From the graph obtained by plotting the logarithm of the vapour pressure against the reciprocal of the absolute temperature, read off the values of the vapour pressure at intervals of 5°–10°. By means of these values calculate the molar heat of vaporization at different temperature intervals, using the equation given on p. 67. (The molar heat varies with the temperature of vaporization.)

From one known value, p_1, of the vapour pressure, at temperature T_1, calculate, by means of the equation on p. 67, the vapour pressure p_2, at the temperature $T + \Delta T$, where $\Delta T = 1°–2°$. The temperature coefficient of vapour pressure, $\dfrac{\Delta p}{\Delta T}$, can then be calculated, also the change of boiling-point with pressure, $\dfrac{\Delta T}{\Delta p}$.

II. Method of Smith and Menzies.—The method of determining vapour pressures introduced by Smith and Menzies [1] is somewhat simpler than that of Ramsay and Young, and is especially useful when only a small quantity of the liquid is available.

The liquid to be investigated is placed in a small bulb-tube A (Fig. 33), which is then attached by thread to the thermometer T. (The bulb of A is about 1 cm. in diameter and is blown on a capillary tube 3–4 cm. in length and with a lumen of 1–1·5 mm.) The thermometer and bulb are fitted by means of a rubber bung into a tube B, which is nearly filled with a liquid of considerably higher boiling-point than that under investigation. It is advisable, also, to use a liquid in B with which the liquid under investigation is only slightly miscible. Tube B is connected by means of C with a manometer and large pressure-regulating bottle, as shown in Fig. 32. The temperature of the liquid in B is regulated by placing the tube in a bath of suitable liquid contained in a beaker D.

EXPERIMENT.—*Determine the Vapour Pressure of Benzene.*

The bulb-tube A is two-thirds filled with benzene, attached to the thermometer T, and the apparatus fitted together as shown in Fig. 33. Water, or a solution of calcium chloride, may be used in the tube B, and also in the

[1] *J. Amer. Chem. Soc.*, 1910, **32**, 897, 907.

bath D. Tube C is connected with the manometer and pressure-regulating bottle. When the apparatus has been assembled, partially exhaust by means of a pump in order to test for leaks. If the apparatus is satisfactory, admit air again and adjust the temperature of the bath to, say, 15°. Stir the bath liquid well,[1] and keep the temperature as steady as possible. When the temperature of the liquid in B has become constant, reduce the pressure in the apparatus by means of a pump. As the pressure falls, air escapes
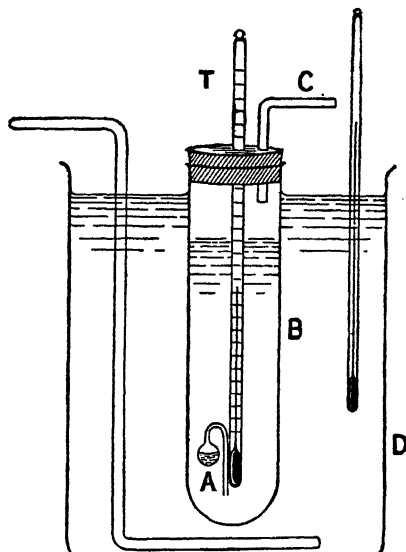
FIG. 33.

from the bulb-tube A. Later, the liquid in A will begin to boil and a stream of bubbles will escape from the capillary of A. When this occurs, close the tap G (Fig. 32). Allow the liquid in A to boil for a short time in order that air may be completely expelled from the bulb. Now open the tap H (Fig. 32) and allow air to enter the apparatus through a piece of tubing which has been drawn out to a very fine capillary. If the capillary has been made sufficiently fine, the pressure within the apparatus will increase very slowly.[2]

[1] A mechanical stirrer may be fitted in place of the hand stirrer.
[2] Instead of the capillary tube H, one may also have two taps on the tube, and by opening and shutting these taps alternately, the pressure in the apparatus may be gradually increased.

While maintaining the temperature of the bath as constant as possible, allow the pressure to increase until the liquid in A just ceases to boil. Close the tap H, read carefully the pressure on the manometer and the temperature indicated by the thermometer T. (The reading of the temperature must be corrected for exposed stem if necessary.) The depth of liquid in the tube B down to the opening of the capillary of the bulb-tube A, must also be measured. Knowing the density of the liquid (this need be determined only approximately by means of a hydrometer), the pressure of the measured head of liquid in millimetres of mercury can be calculated. The value of this added to the pressure shown by the manometer gives the vapour pressure of the benzene at the temperature registered by T.

The temperature of the bath is now slowly raised by, say, 10°, air being admitted into the apparatus so as to prevent the benzene from boiling excessively. Keep the temperature steady at the new value, and adjust the pressure as before so that the boiling, and consequent rapid escape of bubbles from the bulb tube, just cease. Readings of temperature and pressure to be made as before.

A series of determinations should be made at intervals of about 10° up to the boiling-point of benzene under a pressure of 760 mm.

The vapour pressure of water may also be determined in the same way, using a high-boiling medicinal paraffin as liquid in B.

It has been pointed out that the liquid under investigation should be only slightly soluble in the liquid filling the tube B, and if this is not the case, the vapour pressure cannot be determined sharply by a cessation of the flow of bubbles from A. In this case, a mark should be made on the capillary tube of A by fusing, for example, a thread of coloured glass to the outside of the capillary at a distance of 5–10 mm. from its open end, and the pressure should be noted when the liquid in B rises to this mark on the capillary tube. Since the area of liquid in the capillary tube is very small the surface layer soon becomes saturated with the vapour of the liquid in A, and its level is therefore fixed by the vapour pressure of the liquid in A.

The values of the vapour pressure should be plotted, and the calculations made as described on p. 70.

III. Determination of Vapour Pressure by the Isoteniscope.[1]
—The method is a static one in contrast with those already described, which are dynamic. The *isoteniscope* has the form shown in Fig. 34, the limbs of the ∪-tube being 30–35 mm. in length, and the vertical tube about 24 cm. The bulb is about 2 cm. in diameter, and, for the sake of compactness, the neck of the bulb is bent so that the bulb lies behind the ∪-tube.

In carrying out a determination of the vapour pressure of a liquid, *e.g.* water or benzene, the latter is introduced into the isoteniscope in such amount that the bulb is about half full, and the liquid stands about half-way up the limbs of the ∪-tube. The apparatus is then immersed, to the level of the upper bulb, in a large beaker of water or other suitable heating liquid, and is connected with a manometer and pressure-regulating bottle (Fig. 32). The bath liquid must be stirred well. When the apparatus has attained the temperature of the bath, the pressure is reduced until the liquid in the bulb of the isoteniscope begins to boil. After a short time, when any dissolved or adhering air has been removed, tap G (Fig. 32) is closed and air

FIG. 34.

allowed to enter very slowly through H, until the level of liquid is the same in the two limbs of the ∪-tube. The temperature of the bath and the pressure must then be read carefully.

Further determinations of the vapour pressure are then carried out, as before, at a series of higher temperatures.

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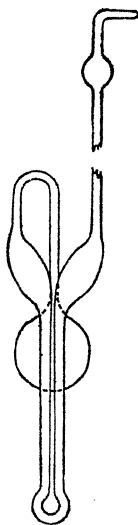
[1] Smith and Menzies, *J. Amer. Chem. Soc.*, 1910, **32**, 1412.

CHAPTER VI

VISCOSITY AND SURFACE TENSION

A.—VISCOSITY

WHEN a liquid flows through a narrow tube, the velocity of flow will depend, in the first place, on the force which produces the flow. All parts of the liquid, however, do not move through the tube with the same velocity, but the layers next the sides of the tube move more slowly than the middle layers. There is thus a shearing, or a movement of the different layers past one another in the direction of flow; and this displacement of the different layers relatively to one another is opposed by the internal friction or *viscosity* of the liquid. We can, therefore, regard the liquid as made up of a number of concentric tubes sliding past one another like the tubes of a telescope.

When the liquid is moving through the narrow tube, there will be a constant difference in velocity between the different tubes of which we have regarded the cylinder of liquid made up, and it has been found that the force per unit area which is necessary to maintain this condition is proportional to the difference of velocity, v, of two adjacent tubes (or their relative velocity of displacement), and inversely proportional to their distance, x, apart, *i.e.*—

$$\text{Force} = \eta \times \frac{v}{x}$$

where η is a constant known as the *coefficient of viscosity*. This coefficient of viscosity is numerically equal to the tangential force per unit area required to maintain unit velocity of displacement of two parallel planes at unit distance apart, the space between the planes being filled with the viscous fluid.

For the flow of a homogeneous liquid through a capillary

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tube, the expression (Poiseuille's formula) has been deduced—

$$\eta = \frac{\pi p r^4 t}{8Vl}$$

where p is the driving force, r is the radius of the tube, t is the time required for the volume, V, of liquid to flow through the tube of length l. This formula holds strictly, however, only when the velocity of the liquid on leaving the tube is zero; and when this is not the case, a correction for the kinetic energy of the liquid must be introduced. It is, therefore, better in practice to use an apparatus of such a form that the value of this correction is reduced to such an extent as to be negligible. For our present purpose no account need be taken of it.

The apparatus now generally employed for the determination of the viscosity of liquids is the Ostwald modification of Poiseuille's apparatus,[1] shown in Fig. 35. It consists of a fine capillary tube db (about 10 cm. long and 0·4 mm. bore), through which a definite volume of liquid—namely, that contained between the two marks c and d—is allowed to flow under the force of its own weight. A definite volume of liquid is introduced into the larger bulb e through the tube f, by means of an accurately calibrated pipette, and is then, either by blowing through f or by sucking at a, forced up through the capillary until the level of the liquid rises above the upper mark c. The liquid is then allowed to flow back through the capillary, and the time required for the surface of the liquid to pass from the mark c to the mark d is noted.
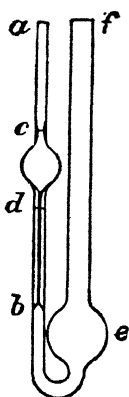
FIG. 35.

The force driving the liquid through the capillary is equal to $h \times d_1 \times g$, where h is the mean difference of level of the liquid in the two limbs of the tube, d_1 is the density of the liquid, and g is the acceleration of gravity. If, now, the *same volume* of a second liquid is introduced into the tube, the mean difference of level of the two liquid surfaces will also be h, so that the driving force is now $h \times d_2 \times g$; or the driving force is proportional to the densities of the two

[1] For a discussion of the viscosity of liquids, see Bingham, *Fluidity and Plasticity*; Hatschek, *The Viscosity of Liquids*; Dunstan and Thole, *The Viscosity of Liquids*; G. Barr, *Viscometry*.

liquids. But we have already seen that the viscosity, η, is equal to $\frac{\pi r^4}{8Vl} \cdot pt$; *i.e.* for a given apparatus and the same volume, V, of liquid, η is proportional to the driving force and to the time of outflow. Hence—

$$\frac{\eta_2}{\eta_1} = \frac{h \cdot d_2 \cdot g \cdot t_2}{h \cdot d_1 \cdot g \cdot t_1} = \frac{d_2 t_2}{d_1 t_1}$$

This expression gives the viscosity of the second liquid relatively to that of the first. For many purposes only the relative viscosity of a liquid is required, and as comparison viscosity that of water at some particular temperature, either 0° or 25°, is generally chosen. It is, of course, easy to obtain the coefficient of viscosity of a liquid in absolute units, by substituting in the above equation the value in absolute units of η_1, the coefficient of viscosity of the comparison liquid. The unit of viscosity in C.G.S. units is known as a *poise* (from Poiseuille).

Before being used, the viscosity tube must be thoroughly cleaned, so that there are no obstructions in the capillary, and the liquid must run clean from the glass without leaving drops behind. To secure this, the tube should be kept filled for some hours with a warm solution of chromic acid (sulphuric acid and potassium dichromate), and then thoroughly washed with distilled water, which may be drawn through the tube with the aid of a filter pump. The tube is then dried by heating in a steam oven, and drawing air, *filtered through cotton-wool*, through the tube ; or it may be washed with alcohol and ether, and the latter removed by a current of air.

As the viscosity of a liquid varies greatly with the temperature (roughly 2 per cent. per degree), the tube and liquid must be kept at a constant temperature during the measurement. The tube is therefore suspended in a bath, the temperature of which can be regulated to within 0·1°. As it is necessary to watch the flow of liquid, the thermostat must be transparent, or have transparent sides. One may therefore use a large beaker or a metal bath with transparent sides fitted with a thermo-regulator and stirrer. The viscosity tube must be supported in a perpendicular position, and should be immersed in the liquid of the thermostat to such a depth that the upper mark c is well beneath the surface.

For determining the time of outflow, a stop-watch, reading direct to 0·2 second, should be used.

EXPERIMENT.—*Determine the Relative Viscosity of Benzene, and the Influence of Temperature on the Viscosity.*

Set up a transparent thermostat and stirrer, and adjust the temperature to 25·0°. Having thoroughly cleaned a viscosity tube, introduce into the larger bulb e, by means of a calibrated pipette, a volume of water, recently boiled and allowed to cool, sufficient to fill the bend of the tube and half, or rather more than half, of the bulb e. Fix the viscosity tube in the thermostat, and after allowing 10–15 minutes for the temperature of the tube and water to become constant, attach a piece of rubber tubing to the narrower limb of the viscosity tube, and suck up the water to above the mark c. Then allow the water to flow back through the capillary, and determine the time of outflow by starting the stop-watch as the meniscus passes the upper mark c, and stopping it as the meniscus passes the lower mark d. Repeat the measurement four or five times, and take the mean of the determinations. If the time of outflow is about 100 seconds, the different readings should not deviate from the mean by more than 0·1–0·3 second. Greater deviations point to the capillary tube being dirty.

The viscosity tube and pipette must now be dried, and an equal volume of pure benzene introduced into the tube in place of the water. Readings of the time of outflow are then made as in the case of water. The density of benzene at 25° compared with that of water at 25° (see p. 64) is then determined, and the viscosity of benzene, relative to that of water at 25°, is calculated by means of the formula—

$$\eta_{\text{(benzene)}} = \frac{(\text{time} \times \text{density})_{\text{benzene}}}{(\text{time} \times \text{density})_{\text{water}}}$$

To determine the influence of temperature on the viscosity, the time of outflow and the density (compared with that of water at 25°) should be determined at intervals of 5° between the temperatures of 25° and 50°. The values are then plotted on squared paper, and the value of the temperature coefficient $\frac{\Delta\eta}{\Delta t}$ for each range of 5° calculated.

By plotting the fluidities $\left(=\frac{1}{\eta}\right)$ against the temperature, curves are obtained which approach more nearly to straight lines.

Calculations.—From the values of the relative viscosity, determined above, calculate the viscosity coefficient of benzene in C.G.S. units, the viscosity coefficient of water at 25° being taken as equal to $8 \cdot 95 \times 10^{-3}$ poises. Plot the logarithms of the viscosity values, (log η), against $1/T$, when a straight line graph should be obtained.[1] From this graph, read off the values of η at 10°, 20°, 30°, 40° and 50°, and compare them with those given in the following table.

VISCOSITY COEFFICIENT OF BENZENE IN ABSOLUTE UNITS.

Temperature.	$\eta \times 10^3$
10°	7·59
20°	6·49
30°	5·62
40°	4·92
50°	4·37

Differences should not exceed 1 per cent.[2]

Further Work.—The viscosities of other liquids, *e.g.* methyl alcohol, ethyl alcohol, carbon tetrachloride, toluene, etc., may be determined at different temperatures, and the graphs of $\log_{10}\eta$ against $1/T$ compared. (At lower temperatures, the graphs, in the case of associated liquids, are not straight lines.) For table of viscosity coefficients, see Appendix.

Viscosity-Constitution Constants.—It has been found [3] that for a large number of organic liquids the equation $\log_{10} (\log_{10}\eta) = md - 2 \cdot 9$ is valid. In this expression, η is the viscosity coefficient in *millipoises*, m is a constant characteristic of the liquid, d is the density in grams per ml. The viscosity-constitution constant, I, obtained by multiplying m by the molecular weight M, is equal to the sum of atomic and structural constants, some of the values of which are given in the following table :—

ATOMIC AND STRUCTURAL VISCOSITY-CONSTITUTION CONSTANTS.

CH_2	=	55·6	N	=37
H	=	2·7	NO_2	=80
C	=	50·2	Cl	=60
O	=	29·7	$\models$	=−15·5
OH	=	57·1	5-C ring	=−24
COO	=	90	6-C ring	=−21
COOH	=104·4			

Side group on a 6-ring=− 9 (if mol. weight of group is less than 17).
    ,,   ,,   ,, = −17 (if mol. weight of group is greater than 16).

[1] Andrade, *Nature*, 1930, **125**, 309, 582.
[2] Where the highest accuracy is not required, the viscosity of a liquid can be readily determined by a method due to Scarpa, *Gazzetta*, 1910, **40**, 271. See also Farrow, *J. Chem. Soc.*, 1912, **101**, 347. This method does not involve determination of the density.
[3] M. Souders, Jr., *J. Amer. Chem. Soc.*, 1938, **60**, 154.

Exercise.—Determine the density and visosity coefficient (in millipoises) of a number of compounds, *e.g.* benzene, toluene, ethyl ether, acetone, nitrobenzene, ethyl acetate, and calculate the value of the viscosity-constitution constants by means of the expression

$$I = \frac{M}{d} [\log_{10}(\log_{10}\eta) + 2 \cdot 9].$$

Compare the values obtained with those calculated from the sum of the atomic and structural constants.

Viscosity of Homogeneous Mixtures.—In the same way as already described, the relative viscosity of homogeneous mixtures of two liquids, *e.g.* benzene and carbon tetrachloride, benzene and ethyl alcohol, chloroform and acetone, may be determined at various concentrations of the components. The solutions are made up by weight, and the viscosity values at a given temperature should be plotted as ordinates against the molar fraction of one of the constituents. By molar fraction there is meant the ratio $\frac{n_1}{n_1 + n_2}$, where n_1 is the number of gram molecules of one of the constituents and n_2 the number of gram molecules of the other. Curves of various forms are obtained, the interpretation of which, however, is not quite definite.

Falling-Sphere Viscometer.—In the case of liquids of high viscosity, *e.g.* glycerol, castor oil, solutions of cellulose nitrate, etc., the viscosity can be determined by the rate of fall of a sphere, in accordance with Stokes' law, namely, $v = \frac{2}{9}gr^2 \cdot \frac{S-D}{\eta}$, where v=the velocity of fall in centimetres per second, g=acceleration due to gravity (981 cm./sec.[2]),[1] r=the radius of the sphere, S=density of the sphere, D=the density of the liquid. For a sphere falling axially in a cylinder of liquid of radius R, the equation becomes

$$v = \frac{2}{9}gr^2 \cdot \frac{S-D}{\eta(1 + 2 \cdot 4r/R)}$$

$$\text{or} \quad \eta = \frac{2}{9}gr^2 \cdot \frac{S-D}{v(1 + 2 \cdot 4r/R)}$$

The apparatus devised by W. H. Gibson and L. M. Jacobs [2]

[1] The value of g varies with the locality and when this factor enters into a calculation, the local value should be used. A few values of g for different localities are given in the Appendix.

[2] *J. Chem. Soc.*, 1920, **117**, 973.

is shown in Fig. 36. The fall-tube A, having an internal diameter of about 2 cm. and a total length of about 29 cm., has five rings etched round it at distances of 5 cm. Passing centrally through a rubber stopper in the mouth of A is a tube C, 3 mm. in internal diameter, the end of which reaches to the uppermost ring on A. A small hole is blown in the side of C just below the lower end of the stopper. The liquid, the viscosity of which is to be determined, is placed in tube A, so as to rise about 3 cm. above the uppermost ring, and the tube is supported in a tall cylinder filled with water and provided with a thermometer T, and stirrer S. The temperature is regulated by the addition of hot or cold water.
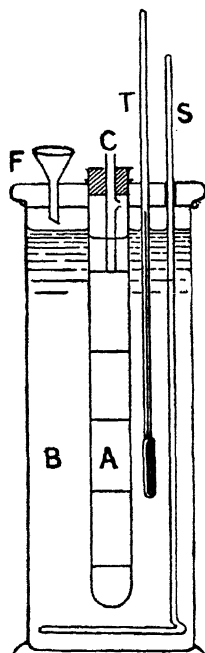
FIG. 36.

EXPERIMENT.—*Determine the Viscosity of Castor Oil.*

After determining the internal diameter of the tube A by means of callipers and accurately measuring the distance between the second and the fifth rings, the apparatus is fitted up as shown in Fig. 36. Castor oil, the density of which has been determined, by means, say, of a Westphal balance or a hydrometer, is poured carefully into the tube A so as to rise about 3 cm. above the uppermost ring, and the rubber stopper with tube C is inserted. The temperature of the water in cylinder B is regulated to, say, 20°. After allowing 20–30 minutes for the temperature of the castor oil to become uniform, a small steel ball (such as is used in ball-bearings) about 0·15 cm. in diameter (the diameter having been determined by means of a micrometer screw gauge), is dropped in through the tube C. By means of a stop-watch, determine the time of fall of the ball between the second and the fifth marks (a distance of 15 cm.). Repeat this determination with at least two other balls of known diameter. The velocity, in cm. per sec., is obtained by dividing the distance by the mean time of fall t, and the viscosity calculated by means of the formula given on p. 79.

The density of the steel balls may be determined by

means of a specific gravity bottle. The dry bottle is first weighed alone and then about one-third full of the steel balls. The difference gives the weight of the balls. The bottle with the balls still in it is filled up with distilled water, taking care that no air is entangled among the balls, and the stopper inserted. The bottle is placed in a bath at 20°, and when the temperature is constant, excess of water is removed from around the capillary in the stopper (leaving, however, the capillary full of water) and the bottle removed from the bath, wiped dry, and weighed. By subtracting from this total weight, the weight of the empty bottle and of the steel balls, the weight of the water present is obtained. Knowing the density of water at 20°, its volume can be calculated, and if this be subtracted from the total internal volume of the bottle, the volume of the known weight of steel balls is obtained, and therefrom the density of the steel can be calculated. The internal volume of the bottle can be obtained by weighing it full of water, as explained on p. 21.

Using steel balls ($S=7.65$), Gibson and Jacobs found for castor oil ($D=0.96$) at 20° the viscosity value 9.88 in c.g.s. units.

<h2 style="text-align:center">B.—SURFACE TENSION.[1]</h2>

A molecule in the body of a liquid is equally attracted in all directions, but a molecule in the surface layer is subject to an unbalanced force acting inwards at right angles to the surface ; and this force, acting perpendicularly to a section of the surface 1 cm. long, is called the *surface tension.* Its value is generally expressed in dynes per centimetre. Here only the surface tension which exists between a liquid and its vapour or a liquid and air will be considered.

The value of the surface tension depends on the nature of the liquid and also on the temperature, rise of temperature being accompanied by a decrease of the surface tension.

The product $\gamma \cdot V^{\frac{2}{3}}$ or $\gamma(Mv)^{\frac{2}{3}}$, where V is the molecular volume, M is the molecular weight and v is the specific volume, is called the *molecular surface energy,* and it has been shown by Ramsay and Shields that the molecular surface energy is a linear function of the temperature. The difference of molecular surface energy at two temperatures,

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[1] See Willows and Hatschek, *Surface Tension and Surface Energy* ; Adam, *Physics and Chemistry of Surfaces.*

therefore, divided by the difference of temperature, is constant. Moreover, the numerical value of this constant is approximately the same for different non-associated liquids, viz. 2·12 when γ is measured in absolute units. For different non-associated liquids, therefore, one has the expression

$$\frac{\gamma_1(Mv_1)^{\frac{2}{3}}-\gamma_2(Mv_2)^{\frac{2}{3}}}{t_2-t_1}=2\cdot12$$

The molecular surface energy is therefore a *colligative property*, and can be used for the determination of molecular weights. In this way it has been found that in the case of a number of liquids, more especially liquids containing the hydroxyl group, the value of the above expression, when calculated by means of the normal value of the molecular weight, is less than 2·12 ; and in order to obtain this value, it is necessary to multiply the normal molecular weight of the substance by a factor x greater than unity. This factor is called the *association factor*, and gives the number of times the mean molecular weight of the liquid is greater than the normal molecular weight.[1]

Parachors.—From the relationship, $\gamma=C(D-d)^4$, discovered by D. B. Macleod,[2] it follows that, for a given liquid, the expression $\dfrac{M}{(D-d)}\cdot\gamma^{\frac{1}{4}}$ should be constant, independent of the temperature. In this expression, γ is the surface tension, D is the density of the liquid, and d is the density of its saturated vapour, all measured at the same temperature. Since, at ordinary temperatures, d is small compared with D, one may write $\dfrac{M}{D}\cdot\gamma^{\frac{1}{4}}=[P]$, where $[P]$ is a constant, known as the *parachor*,[3] and is a measure of the molecular volume at temperatures at which different liquids have the same surface tension. The parachor, it has been found, is an additive property, so that the value for a given molecule can

[1] A more exact expression for the variation of molecular surface energy with the temperature has been obtained by M. Katayama (*Sci. Rep. Tohoku Univ.*, 1915, **4**, 373). It has also been shown that the above Ramsay-Shields method of determining the degree of association of a liquid is not altogether reliable (Jaeger, *Z. anorgan. Chem.*, 1917, **101**, 1), and should be regarded as affording only a qualitative indication of molecular complexity.

[2] *Trans. Faraday Soc.*, 1923, **19**, 38.

[3] Sugden, *J. Chem. Soc.*, 1924, **135**, 1177 ; *The Parachor and Valency*.

be calculated as the sum of a series of atomic or structural constants, of which the following are a few values :—

ATOMIC AND STRUCTURAL PARACHORS.

C	4·8	Non-polar double bond	23·2
H	17·1	Semi-polar double bond	— 1·6
N	12·5	Triple bond	46·6
O	20·0	3-membered ring	16·7
O_2 (in esters)	60·0	4-membered ring	11·6
P	37·7	5-membered ring	8·5
S	48·2	6-membered ring	6·1
Cl	54·3		

The parachor is, however, not merely an additive but quite definitely also a constitutive property.

Surface Tension and Viscosity.—Various relations have been found to exist between the surface tension of a liquid and its viscosity. Thus, it has been shown [1] that $\gamma^{-\frac{1}{4}} = A/\eta + B$, where A and B are constants. Consequently, when $\gamma^{-\frac{1}{4}}$ is plotted against the fluidity, a straight line is obtained. Moreover, Buehler [2] has shown that in the case of compounds for which the parachor is independent of the temperature, the ratio $I/[P] = 1·2$, where I is the viscosity-constitution constant (p. 78) and $[P]$ is the parachor. When, therefore, the surface tension and the viscosity (in millipoises) of a liquid are determined at the same temperature (the density, therefore, being the same), the equation

$$\log_{10}(\log_{10}\eta) = 1·2\gamma^{\frac{1}{4}} - 2·9$$

is found to be valid.

MEASUREMENT OF THE SURFACE TENSION

1. Capillary-rise Method.—One of the most important methods for the measurement of the surface tension of a liquid is the determination of the height to which the liquid rises in a capillary tube.

If γ denotes the value of the surface tension, and h the height in centimetres to which a liquid of density (specific gravity) d rises in a tube of radius r cm., one obtains the expression—

$$\gamma = \tfrac{1}{2}.h.r.d.g$$

[1] Silverman and Reseveare, *J. Amer. Chem. Soc.*, 1932, **54**, 4460.
[2] *J. Physical Chem.*, 1938, **42**, 1207.

where g is the value of gravity (981 dynes).[1]   The value of the surface tension is thus obtained in absolute units (dynes per cm.).

Apparatus.—For the purpose of the following experiments the simple apparatus shown in Fig. 37 may be employed.   The capillary tube (diameter of bore about 0·4 mm.) passes through a cork fixed in the neck of the tube A, in which the liquid to be investigated is placed.   To render the correction for the meniscus sufficiently small, the lower end of A should have an internal diameter of at least 3 cm.,[2] and preferably one of 4–5 cm.   On the capillary tube a millimetre scale is etched ;   or a millimeter scale ruled on glass or opal is attached to the capillary tube.   In order that the scale may not alter its position it is well to allow it to rest on two small glass hooks sealed to the wall of the capillary tube, near its lower end, and to bind the scale to the capillary by fine platinum or nickel wire or by narrow strips of sheet brass.   The height to which the liquid rises in the capillary tube is read off by means of a reading lens, or by a telescope placed at a convenient distance.   The height may also be read more accurately by means of a cathetometer.

EXPERIMENT.—*Determine the Radius of the Capillary Tube.*

The radius of the bore of the capillary tube can be most conveniently determined by measuring the rise of a standard liquid, *e.g.* benzene, in the tube at a given temperature.

Fit up a thermostat with transparent sides, or a . large beaker, filled with water, and regulate the temperature to 0·1° in the neighbourhood of 20°.   Thoroughly clean the capillary tube with chromic acid mixture, wash well with distilled water, then with redistilled methylated spirit, and lastly wash out once or twice with pure benzene.   Place a quantity of pure benzene in the outer tube (Fig. 37), and fix the cork carrying the capillary tube in its place ;   the capillary, however, being drawn so far through the cork that the lower end does not dip into the benzene.   Support

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[1] It is assumed here that the angle of contact between the liquid and glass is zero, and this assumption has been shown to be justified.   The value of g depends on the latitude.

For determinations of the surface tension of liquids by the capillary-rise method, see Richards and Carver, *J. Amer. Chem. Soc.*, 1921, **43**, 827.

[2] Richards and Coombs, *J. Amer. Chem. Soc.*, 1915, **37**, 1656.

the tubes in a perpendicular position in the thermostat, and, after the benzene has taken the temperature of the bath, lower the capillary and scale so as to dip beneath the surface of the benzene. By gently blowing and sucking through the tube, C, cause the benzene to pass up and down the capillary, so that the walls of the latter may become completely wetted. By means of a telescope or cathetometer placed at a convenient distance, read the position on the scale of the benzene meniscus in the wider tube and in the capillary. Three or four readings should be made, both after the benzene has been made to rise above (by blowing through C), and made to fall below (by sucking through C), its final position. The different readings should not differ from the mean value by more than $\pm 0 \cdot 2$ mm. from one another. Greater deviations point to the capillary tube being dirty.

Having determined the rise of liquid at $20°$, repeat the determination at, say, $40°$; the temperature being again kept constant to within $0 \cdot 1°$. As the rise will in this case not be so great as in the former case, the capillary must be lowered farther into the benzene, in order that the meniscus in the capillary shall stand at the same point as before. If necessary, a further quantity of benzene should be poured into the outer tube.

From these two determinations of the rise of benzene, the radius of the capillary at the point at which the meniscus stood can be calculated from the equation

FIG. 37.

$\gamma = \frac{1}{2}.h.r.d.g$, provided that we know the values of γ and of d, at the temperatures of the determinations.

The value of γ can be read from a curve obtained by plotting the values of the surface tension given in the Appendix, and the value of the density of benzene can be calculated by means of the equation : $d_t = d_0 + 10^{-3}\alpha(t-t_0) + 10^{-6}\beta(t-t_0)^2$. In this expression $d_0 = 0 \cdot 90005$; $\alpha = -1 \cdot 0636$, $\beta = -0 \cdot 0376$.
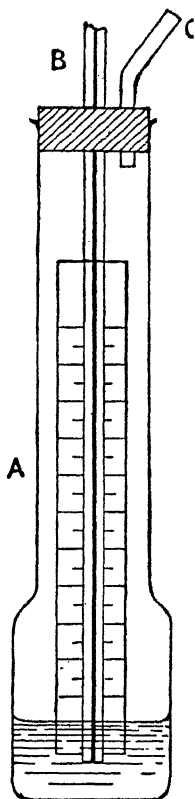
The mean of the values obtained at the two temperatures may be taken as the true value of the radius.

EXPERIMENT.—*Determine the Molecular Surface Energy and the Association Factor of Ethyl Alcohol.*

Having thoroughly cleaned the outer tube and capillary (the latter should be washed out once or twice with pure alcohol before use), the apparatus is again fitted together and fixed in the thermostat, which should be regulated for a temperature of about 20°. The amount of alcohol placed in the outer tube should be regulated so that the meniscus in the capillary stands at the same point as in the case of benzene. The capillary rise is determined in the same way as before; several readings being taken both with falling and with rising meniscus.

A similar set of readings should be taken at a higher temperature, say, about 40°.

The density (specific gravity) of the alcohol at the same temperatures as above must also be determined.

From the value of the capillary rise, the density, and the radius of the capillary as determined in the preceding experiment, the value of the surface tension at each temperature can be calculated. Compare the results with the values obtained by plotting the following values :—

SURFACE TENSION OF ALCOHOL.

Temperature.	γ
10·0°	23·14
20·0°	22·27
40·0°	20·60
60·0°	19·01

An error of 0·5 per cent. may be allowed in the values of the surface tension.

Additional Experiments and Calculations.—The surface tension of other liquids, *e.g.* methyl alcohol, toluene, chloroform, ethyl ether, acetone, nitrobenzene, ethyl acetate, benzyl alcohol, acetaldehyde, paraldehyde, may be measured at two temperatures and the values of the molecular surface energy calculated. Consider which of the liquids is associated, and in the case of associated liquids, calculate the degree of association, x, from the expression $x = \left(\dfrac{2 \cdot 12}{k}\right)^{\frac{3}{2}}$, where k is the temperature coefficient of molecular surface energy.

By means of the expression $\dfrac{M}{D} \cdot \gamma^{\frac{1}{4}}$, calculate also the value of the parachor, and compare with the sum of the atomic values (p. 83).

From previous determinations of the viscosity, find the value of $I/[P]$ (p. 83), at a given temperature.

2. Drop-Weight Method.—The value of the surface tension can also be obtained by determining the weight of the drop of liquid which falls freely from the end of a tube. The surface tension of the liquid, it was thought, could be calculated by means of the expression, $\gamma = W/2\pi r = mg/2\pi r$, where W is the weight and m is the mass of the drop. It has been shown,[1] however, that this equation is incorrect, but that correct values of the surface tension can be obtained by using the expression $\gamma = \dfrac{mg}{r} \cdot F$, where F is a function of

$\dfrac{v}{r^3}$, v being the volume of a drop and r the radius of the end of the tube. Values of F are given in the following table (*International Critical Tables*) :—

v/r^3	F	v/r^3	F	v/r^3	F
10·29	0·23976	2·637	0·26224	1·2109	0·26407
8·190	0·24398	2·3414	0·26350	1·124	0·2632
6·662	0·24786	2·0929	0·26452	1·048	0·2617
5·522	0·25135	1·8839	0·26522	0·980	0·2602
4·653	0·25419	1·7062	0·26562	0·912	0·2585
3·975	0·25661	1·5545	0·26566	0·865	0·2570
3·433	0·25874	1·4235	0·26544		
2·995	0·26065	1·3096	0·26495		

Apparatus.—For the measurement of surface tension by the drop-weight method, the apparatus devised by J. L. R. Morgan has proved very satisfactory.[2] It consists of two small weighing bottles, A and B (Fig. 38), through the stoppers of which pass the limbs of an inverted capillary $\bigcup$-tube, of about 0·2 mm. bore. One of the limbs of the tube is about 1 cm. longer than the other. The wall of the shorter limb, to a distance of 0·5–1 cm. from the end, is accurately ground to cylindrical form and the end of this tube must have a sharp edge and be polished smooth and

[1] See Harkins and Humphrey (*J. Amer. Chem. Soc.*, 1916, **38**, 228), and Harkins and Brown (*ibid.*, 1919, **41**, 499) ; Adam, *Physics and Chemistry of Surfaces.*

[2] *J. Amer. Chem. Soc.*, 1911, **33**, 349.

at right angles to the side. The tubes D and D′ are ventila-
tion tubes, by which also the apparatus may be suspended
in a thermostat. The weighing bottles A and B are fixed
by a stopper in a wider tube which acts as an air jacket.

Measurement of the Surface Tension.—The end of the
U-tube with clean and polished dropping tip is fixed in
position in the bottle B, the weight of which has been deter-
mined. The other limb of the U-tube is then fixed in the
bottle A, which contains a quan-
tity of the liquid under inves-
tigation. The outer air-jacket
tube is fixed in position, as
shown, and the apparatus placed
in the thermostat, so that the
capillary U-tube is entirely im-
mersed. By means of a small
rubber bulb attached to the end
of the ventilation tube D′ liquid
is prevented from entering the
capillary in A, the compression
of the rubber bulb being con-
trolled by a screw. After, say,
30 minutes, when the apparatus
has taken the temperature of the
bath, liquid is sucked slowly
from A through the capillary
tube, and the drop allowed to
remain on the end of the tube
for several minutes in order to
saturate the air in B with vapour.
The drop is then allowed to grow
very slowly to its maximum size
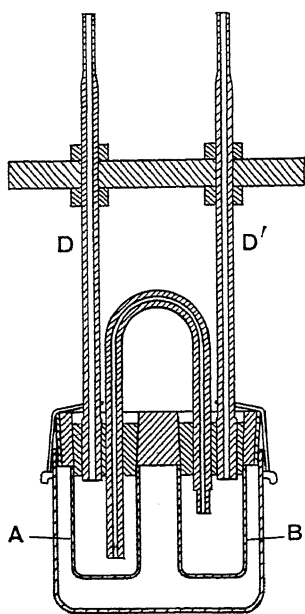
FIG. 38.

and drop from the end of the tip. Twenty-nine other drops
are then allowed to form and drop, the rate being such that
each drop is allowed at least 1 minute to form. When 30
drops have been collected, the liquid in the capillary is forced
back into A, the weighing bottle B removed, stoppered,
dried and weighed, the usual precautions being observed.
The weight of 30 drops plus vapour is thus obtained. The
weighing bottle is then dried, placed once more in position
and drops of liquid collected as before. This time, however,
five drops only are collected. A sixth drop is allowed to
form and to remain on the end of the tube until the total

time of the experiment is the same as in the previous case. The sixth drop is then forced back, and the weight of the 5 drops and vapour determined. This weight subtracted from that for the 30 drops gives the weight of 25 drops, and from this the weight of 1 drop can be calculated. From the weight of a drop and the density of the liquid, the volume of a drop can be obtained; and the radius of the tip can be measured by means of a microscope and scale. The surface tension is then calculated by means of the expression $\gamma = \dfrac{mg}{r} \cdot F$ (p. 87).[1]

Traube's Stalagmometer.—For the determination of the surface tension by the drop method, the Traube stalagmometer [2] may also be used, especially for relative measurements. A diagram of the apparatus is shown in Fig. 39. The dropping-tube or stalagmometer, A, consists of a capillary tube the end of which is flattened out (in order to give a larger dropping surface) and the surface is then carefully ground flat and polished. The capillary is sealed on to a tube of wider bore on which a bulb is blown, and on the stem of the tube two marks are etched, one above and one below the bulb. The determination of the surface tension then consists in counting the number of drops which fall from the end of the stalagmometer while the level of the liquid falls from the upper to the lower mark. To increase the accuracy of the readings, the tube above and below the bulb is marked with a scale. With the help of this, fractions of a drop can be estimated, with an accuracy of 0·05 of a drop, by first determining how many scale divisions correspond to *one* drop. The velocity of flow of the liquid must be regulated so that the number of drops per minute does not exceed 15.
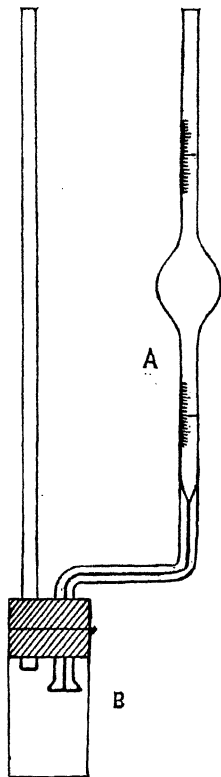
FIG. 39.

The ratio of the surface tensions of two liquids is given by the expression: $\gamma_1/\gamma_2 = n_2 d_1 / n_1 d_2$, where n_1 and n_2 are the numbers of

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[1] For determinations of the surface tension by the drop method, see Morgan, *J. Amer. Chem. Soc.*, 1911, **33**, 349, and later volumes; Harkins and Brown, *ibid.*, 1916, **38**, 246; 1919, **41**, 499; Bircumshaw, *J. Chem. Soc.* 1922, **131**, 887.

[2] *Ber.*, 1887, **20**, 2644, 2824.

drops yielded by the same volume of liquid, and d_1 and d_2 are the densities of the liquids.

In order that the determinations may be carried out at constant temperature, the end of the stalagmometer is passed through a rubber stopper which fits into the neck of a small tube or bottle B (Fig. 39). The apparatus may then be placed in a thermostat.

Different determinations of the drop number should not vary by more than 0·3–0·5 drop.

3. Maximum Bubble Pressure Method.—For the determination of the surface tension of liquids over a range of temperature, especially when only small amounts of liquid are available, the method of maximum pressure in bubbles
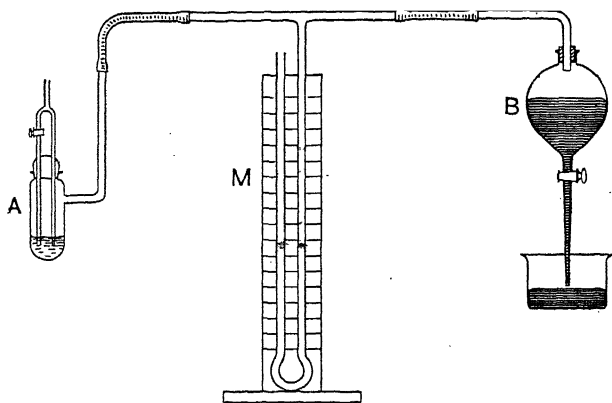
FIG. 40.

is very convenient, and has been extensively employed in calculating the parachor. The technique of this method has been improved and simplified by Sugden.[1]

The method consists in comparing the pressures, P_1 and P_2, required to liberate bubbles from two tubes of different radii, immersed to the same depth in a liquid; and it has been shown that the surface tension of the liquid is given by the equation—

$$\gamma = A(P_1 - P_2)\left(1 + 0.69r_2\frac{gD}{P_1 - P_2}\right),$$

where A is a constant for the particular apparatus, r_2 is the radius of the larger tube, measured in cm., g is the accelera-

[1] *J. Chem. Soc.*, 1922, **121**, 864; 1924, **125**, 27. For a discussion of the theoretical basis of the method, see the papers by Sugden or Adam's *Physics and Chemistry of Surfaces.*

tion due to gravity ($=981$ cm./sec.^{2}), and D is the density of the liquid.

The arrangement of the apparatus is shown in Fig. 40. It consists of a bubbler, A, a manometer, M, and a mercury aspirator, B. Through the stopper of the bubbler (Fig. 41) there pass two tubes, one of which is drawn out to a fine capillary at its lower end. The other has a diameter of about 3–4 mm., and is cut off accurately at right angles with the inner edge sharp and free from splinters. The capillary is made by drawing out a piece of quill tubing, and its bore should be such that when air bubbles are drawn from the tip, immersed in benzene, the pressure difference shown on the manometer lies between 4 and 10 cm. of ethyl alcohol. This corresponds to a capillary ~~diameter~~ lying between 0·01 and 0·005 cm. The capillary must be tested before use.

Ethyl alcohol, coloured with fuchsine or with methylene blue, is used as manometric liquid. From the known value of the density of alcohol at the temperature of the surroundings (determined by means of a thermometer placed near the pressure gauge), the pressure in dynes per sq. cm., corresponding to different gauge readings, can be calculated.

The mercury aspirator may be formed from a 250 ml. separating funnel, the lower end of the stem being drawn out to a point, and the rate of flow of the mercury should be such as to cause bubbles to issue from the capillary tube at the rate of about 1 per second. The column of mercury in the stem of the aspirator, should be continuous.

Measurement of the Surface Tension.—After the apparatus has been assembled, it is necessary, first of all, to determine the constant, A, of the apparatus. This is done with the help of benzene, the surface tension of which is accurately known.

Pure, re-distilled benzene is placed in the bubbler and the cap then placed in position so as to form a tight joint. The ends of the tubes must be about 1 cm. below the surface of the benzene. The bubbler is placed in a thermostat at 20·0° and connected with the manometer and aspirator by means of pressure tubing. The tap on the bubbler is opened and mercury is allowed to flow from the aspirator
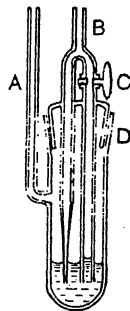
so as to draw bubbles from the end of the wider tube. As bubbles are formed, the pressure rises to a maximum and then decreases suddenly as the bubble is detached. The maximum pressure is read off on the manometer by means of a cathetometer.[1] The wider tube is now closed and bubbles formed at the tip of the capillary tube, at the rate of about 1 per second. The manometer pressure is again read off. The radius r_2, of the wider tube is measured in centimetres by means of a microscope and scale, and the density of benzene can be determined, or found from the tables. (The density of benzene at $20° = 0.87876$.) The surface tension of benzene at $20°$ has the value 28.88 dynes per cm., and at other temperatures is given by the expression

$$= 70.26\left(1 - \frac{T°}{560}\right)^{1.20}$$

By inserting the appropriate values in the expression, $\gamma = A(P_1 - P_2)\left(1 + 0.69r_2\dfrac{g \cdot D}{P_1 - P_2}\right)$, the value of A can be calculated.

After having determined the apparatus constant, A, the surface tension of various liquids (see p. 86) may be determined at different temperatures, and the parachor of the liquid calculated.

4. Torsion Balance Method.—In many cases, *e.g.* biological fluids, colloidal sols, etc., the surface tension can be most satisfactorily determined by means of the torsion-balance method. In the apparatus as improved by du Nouy [2] (Fig. 42), a platinum ring, 4 cm. in circumference, hangs from the end of the beam C, and after the ring has been dipped under the surface of the liquid, one measures, by the torsion of the wire to which the beam C is attached, the force required to raise the ring out of the surface of the liquid. The amount of the torsion is measured by the angle through which the pointer B moves over the scale engraved on the disc. Determinations can be rapidly made with small quantities of liquid (1 ml.).

[1] When a cathetometer is not available, the pressures may be read, by means of a lens or telescope, on a centimetre scale mounted behind the manometer, or calipers with vernier may be used (Haendler and McQuire, *J. Chem. Educ.*, 1937, **14**, 591).

[2] *J. Gen. Physiol.*, 1919, **1**, 521 ; 1925, **7**, 625. For a simple form of apparatus, see Lloyd and Scarth, *Science*, 1926, **64**, 253. See also du Nouy, *Surface Equilibria of Biological and Organic Colloids.*

Determinations may be made of the surface tension of pure liquids or of the solutions previously used. The platinum ring is first thoroughly cleaned by means of a hot sulphuric acid and dichromate mixture, washed with distilled water and heated for a moment in an alcohol flame, or non-luminous Bunsen flame. It is then suspended from the hook on the beam C. The pointer B is set at zero and by means of the screw A, the torsion of the wire is adjusted so that the beam C lies in its normal horizontal
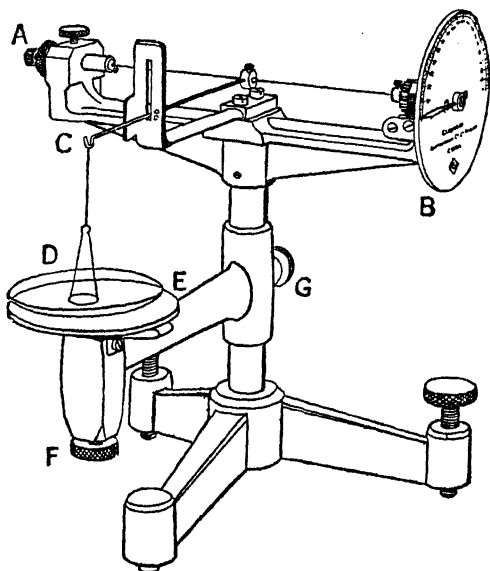
FIG. 42.

position just clear of the arm. The platform with dish containing the liquid under test, is raised until the liquid just touches the ring. The knob which twists the wire is then turned slowly until the ring is suddenly torn from the surface of the liquid, and while this is being done the platform E must at the same time be lowered by means of the screw F so as to keep the beam C always in its normal horizontal position. The position of the pointer on the scale is read when the ring is torn from the surface of the liquid. Make several determinations of this point.

To obtain the value of the surface tension, the scale must be calibrated. This is done by determining the

torsion of the wire with different known weights on the ring. A weighed piece of paper is placed on the ring and weights are added. For each load the wire must be twisted until the beam is in its normal position. The pointer reading on the scale is noted. If the torsion of the wire is proportional to the angle through which the pointer is turned, the weight divided by the scale reading will be the same in each case. If this is not so, the weights must be plotted against scale readings. If the weight in grams is multiplied by the force of gravity, the value in dynes corresponding to a given scale reading is obtained.

The surface tension of a liquid in dynes per centimetre is given by dividing the force in dynes corresponding to the scale reading, by twice the circumference of the ring (because there are two surface films pulling on the ring, one outside and one inside the ring).[1]

Surface Tension of Solutions.—The surface tension of a solution is sometimes greater and sometimes less than that of the pure solvent. In the latter case, the relative lowering of the surface tension is greatest at low concentrations, and is represented, approximately, by the expression $\Delta = \dfrac{\gamma_0 - \gamma}{\gamma_0} = k \cdot c^{\frac{1}{n}}$, where c is the concentration and k and n are constants. That this expression is only approximate is shown by the fact that if the values of log Δ are plotted against the values of log c, the curve is not quite rectilineal.

Determinations should be made of the surface tension of aqueous solutions of ethyl alcohol and of acetic acid, propionic acid and butyric acid at, say, 20°, and at various concentrations up to 1 gram-molecule per litre. Plot the values of the surface tension against the concentration, and also the values of log $\dfrac{\gamma_0 - \gamma}{\gamma_0}$ against log c. Discuss the relative lowering of the surface tension by equimolecular concentrations of the members of the homologous series of fatty acids.

[1] See Harkins and Jordan, *J. Amer. Chem. Soc.*, 1930, **52**, 1751 ; Freud and Freud, *ibid.*, p. 1772.

CHAPTER VII

OPTICAL MEASUREMENTS

A.—Spectrometry

Emission Spectra.—When the white light emitted by an incandescent solid is passed through a prism, it is drawn out into a band of colour, ranging from red, at one end, through orange, yellow, green, blue and indigo, to violet at the other. The spectrum is continuous. When, however, the light emitted by an incandescent gas or vapour is examined by means of a glass prism, a *discontinuous spectrum*, consisting of a number of differently coloured bands or lines, separated by dark spaces, is obtained. Moreover, these bands and lines have, for any given substance, definite positions, so that it is possible, from a determination of the position of the lines, to tell what is the nature of the substance. The determination of the wave-length of the different rays emitted by an incandescent gas is, moreover, of value, not only for the purpose of identifying the substance, but also on account of the relationships which have been found to exist between the spectra of allied elements, and of the light which is thrown on atomic constitution.

FIG. 43.

Light Source.—A gas is most easily raised to incandescence by passing an electric discharge from an induction coil through the gas, contained in a Plücker or Geissler tube, under reduced pressure. In order to obtain stronger illumination, it is best to use an end-on tube (Fig. 43). In the case of hydrogen, it is difficult with an ordinary Geissler tube, to read the G′ line (violet), but by attaching a large bulb to the discharge tube,[1] the latter can be run with a
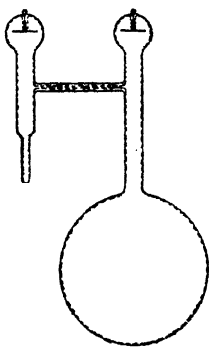
[1] Guild, *Proc. Physical Soc.,* 1915, **28**, 60.

heavier current without any serious rise in the gas pressure taking place owing to the evolution of gas from the electrodes and the walls of the tube. A greater brilliancy of the G' line is thereby secured, and accurate readings of this line are facilitated.

For the examination of the spectrum of neon, the commercial " Osglim " lamp, which may be run off the mains, may be used as light source.

For the examination of the spectra of metals, volatilization of their salts in the Bunsen flame forms a convenient source of illumination, but this method is applicable only in the case of the salts of the alkali and alkaline earth metals.[1]   In order to produce these coloured flames, the chlorides of the metals, because of their volatility, should be used.   These may be
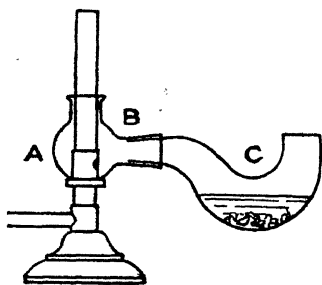
Fig. 44.

employed in the form of solids, and may be supported in the flame by means of clean platinum wire ; or concentrated solutions of the salts, acidified with hydrochloric acid, may be placed in a glass tube and fed into the flame by means of a wick of fibrous asbestos.[2] Suitably coloured flames may also be obtained by supporting in the Bunsen flame small blocks of absorbent asbestos which have been soaked in concentrated solutions of the salts.   A separate block should be used for each salt.

Where a long-enduring flame is desired, use may also be made of the device suggested by Beckmann.[3]   A glass bulb A (Fig. 44), with side tube B, is placed over the tube of the Bunsen burner, so that the side tube is opposite the air inlet of the burner.   Fitting into B by means of a ground joint is another tube C, of the shape shown.   Into the well, formed by the bend in the tube C, is placed a concentrated solution

[1] In other cases, the volatilization of the salts may require the higher temperature of the oxy-hydrogen or oxy-acetylene blowpipe flame, in which case bands due to water vapour make their appearance in the spectrum.   The necessary excitation of the metal atoms may also be produced by forming an electric arc between rods of the metal.   The arc spectra are, in general, richer in lines than the flame spectra.
[2] See also Manley, *Phil. Mag.*, 1923, **45**, 336.
[3] *Z. physikal. Chem.*, 1907, **57**, 641.

of the salt under investigation, together with a few pieces of zinc. A few drops of copper sulphate solution are added in order to coat the zinc with copper. On adding a little dilute hydrochloric acid, hydrogen is generated which, escaping from the solution in fine bubbles, gives rise to a spray. When the gas is burning at the Bunsen, this spray is carried by the current of air into the burning gas and produces the coloured flame.

Electric discharge lamps [1] are now made which give the pure characteristic arc spectra of sodium, cadmium, mercury and zinc. These lamps can be run (through a resistance) off the electric mains and give a high intensity of illumination, many times greater than is obtainable with a Bunsen burner. Although they contain a small quantity of neon, the intensity of the neon lines is relatively very weak.

Other forms of mercury vapour discharge lamps are also available, such as that shown in Fig. 45, which is worked by means of an induction coil. If a silica mercury vapour lamp is used, the eyes must be protected from the harmful ultra-

FIG. 45.

violet rays. In the case of a lamp of ordinary glass, the ultra-violet rays are cut off by the glass.
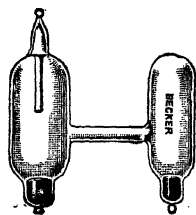
✓ **Spectroscope.**—The apparatus employed for the determination of the wave-length of the lines of a spectrum is called a spectroscope, a simple form of which is shown in Fig. 46. The essential parts of the instrument are : (1) a collimator, A, at one end of which is an adjustable slit and, at the other, a lens by which the rays of light can be rendered parallel, the collimator being clamped in a fixed position ; (2) a prism, P ; (3) a telescope, B, which can be rotated round the central axis ; (4) a tube, D, containing a scale. Measurement of the wave-length of the spectral lines is generally carried out by a method of graphical interpolation, with the help of a number of fixed points. These fixed points are commonly determined by ascertaining the position on a fixed scale of lines of known wave-length.

Adjustment of the Spectroscope.—The telescope is removed from its clamp, and the position of the eye-piece

[1] For example, the " Osira " laboratory lamps made by the General Electric Co.

7

altered until the cross-wires are in focus, the telescope being meanwhile directed to the open sky, or towards a white background.   It is then necessary to focus the telescope for parallel rays, *i.e.* for infinity.   This is done by pointing the telescope at a distant, sharply defined object (say 100 to 200 or more yards distant), and moving the whole tube containing eye-piece and cross-wires until the object appears sharply focussed.   When this is done, the cross-wires and image should not show any relative displacement when the eye is moved in front of the eye-piece.   The telescope is now in focus for parallel light.

The telescope is replaced in its clamp, and is directed to look into the collimator, after the prism has been removed.
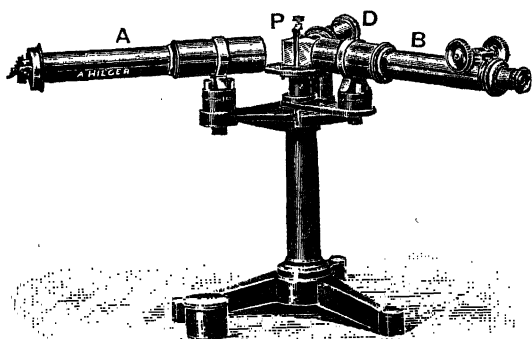
FIG. 46.

The slit of the collimating tube is now illuminated and the distance of the slit from the collimating lens altered until the slit, the image of which should be in the centre of the field of view of the telescope, appears quite sharp.   Since the telescope was focussed for parallel light, it follows that the light coming from the collimator is now parallel.

Now place the prism in its place, with its refracting edge parallel with the slit.   Illuminate the slit by means, say, of a sodium flame or electric discharge lamp (p. 97), and turn the telescope until the image of the slit is seen.   Rotate slowly the table on which the prism stands, or, if the table is fixed, rotate the prism, until it is in the position of minimum deviation.   This is done by rotating the prism, and following the image of the slit with the telescope.   In this way it is found that, as the prism is rotated continuously in one direction, the image of the slit appears to move first in

one direction, and then, at a given point, to stop and move in the opposite direction. The position of minimum deviation is that at which the image changes its direction of movement. This position can then be ascertained more exactly, and the prism fixed. Adjust the slit of the collimator so as to give a narrow sharp line.

A small electric lamp is placed opposite the end of the tube D. The scale is thereby illuminated, and is seen in the telescope by reflection from the face of the prism. Too strong an illumination should be avoided, otherwise difficulty will be found in seeing the weaker spectrum lines.

Turn the telescope until the yellow line of the sodium flame is seen in the centre of the field of view, and focus the scale quite sharply on the face of the prism ; then adjust the position of the scale so that the sodium line [1] coincides with some definite scale mark—say 100. The position on the scale of the spectral lines of mercury and cadmium, or of hydrogen and helium, are then determined, and the scale numbers plotted against wave-lengths.

The wave-lengths of the chief lines in the spectra of these elements are as follows :—

Cadmium.		Mercury.	
Line.	Wave-length in A.	Line.	Wave-length in A.
Red	6438	Yellow	5791
Green	5086	Green	5461
Blue	4800	Violet	4358
Blue	4678	Violet	4047

Hydrogen.		Helium.	
Line.	Wave-length in A.	Line.	Wave-length in A.
C (red)	6563	Red	7065
F (blue)	4861	,,	6678
G' (violet)	4341	Yellow	5876
		Green	4922
		Blue	4713
		Violet	4472

[1] If the dispersive power of the prism is sufficiently great, *two* yellow lines will be seen, the wave-lengths of which are 5896 and 5890 A. respectively. The scale may be adjusted for one of these lines. An Ångström unit (A.) is equal to 1 ten-millionth of a millimetre ($=$0·1mμ), or 1 × 10^{-8} cm.

Having, in the manner described, constructed a spectrum map, as it is called, examine the light emitted when the chlorides of sodium, potassium, lithium and thallium [1] are vaporized in a Bunsen flame, and determine the positions on the scale of the chief spectrum lines. From the spectrum map, read off the corresponding wave-lengths.

One may also examine the spectrum of neon, which is very rich in red rays and shows also a characteristic yellow line at wave-length 5853 A.

The chief lines to be looked for in the case of the salts mentioned above are :—

Chloride of	Colour of line.	Wave-length in Ång-ström units.
Potassium	Red	7699
	,,	7665
	Violet	4047
	,,	4044
Lithium	Red	6708
Sodium	Yellow	5896
	,,	5890
Thallium	Green	5350

The Hilger Wave-length Spectrometer (Constant Deviation Type).—The determination of the wave-lengths of
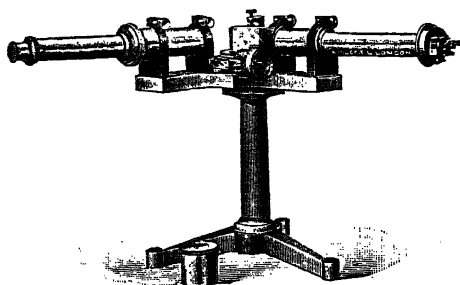
FIG. 47.

spectral lines is rendered very simple by using a spectrometer graduated so as to allow of the wave-lengths being read off directly on a scale. Such an instrument is the Hilger Wave-length Spectrometer (constant deviation type). In this instrument (Fig. 47) use is made of a " constant

[1] The fumes of thallium chloride should not be allowed to pass into the air of the room. Place the flame under a hood.

deviation prism," consisting of a solid piece of glass cut in the form shown in Fig. 48. A ray of light entering the prism at the angle of minimum deviation, travels in the prism in a direction parallel to BD and is reflected from the face AD. It then emerges from the face BC of the prism in a direction at right angles to the incident ray. The collimator and telescope of the instrument are therefore rigidly fixed to the base at right angles to each other. By rotating the turntable carrying the prism the different lines of the spectrum can be brought into coincidence with the spider wire in the telescope, and as the collimator and telescope are
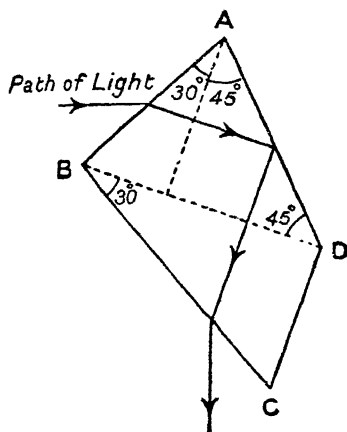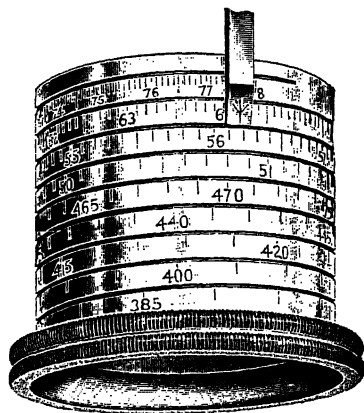
FIG. 48. FIG. 49.

at right angles, the light must have passed through the prism at minimum deviation. The turntable carrying the prism is rotated by means of a fine steel screw, the hardened point of which presses against a polished steel plug in a projecting arm attached to the table. To the screw is fixed a drum (Fig. 49), on which the wave-length of the line under investigation is read off directly as indicated by the index, which travels in a helical slot in the drum.

In order to use the spectrometer, clamp the telescope and collimator firmly in place, keeping the slit of the collimator in a vertical position, so that the image of the slit is parallel to the spider wire in the telescope. Fix the prism also in the position marked on the turntable, by means of the clamp-screw. Be careful not to finger the refracting faces

of the prism, and see that they are quite clean. Focus the spider wire by turning the eye-piece of the telescope and illuminate the slit by means of a sodium flame or electric discharge lamp (p. 97). If the slit is too wide, only one yellow line will be seen, and the slit must be narrowed down by means of the adjusting screw until two narrow lines appear in the telescope. By means of a milled ring on the tube of the telescope the lines may be focussed sharply. The graduated drum is now rotated until the index is at the graduation representing the wave-length 5896. (As it is important in making a reading always to rotate the drum right-handedly, in order that there may always be " pushing contact " between the end of the screw and the turntable arm, the drum should first be set for a wave-length greater than 5896, and then rotated carefully to the right until this wave-length is reached.) Observe now if the spider wire in the telescope coincides with the yellow sodium line of greater wave-length (nearer the red end of the spectrum). If this is so, then the instrument is in proper adjustment; but if not, loosen the prism clamp and move the prism very carefully—the slightest movement will produce a considerable displacement of the line—until the line coincides with the spider wire.[1] If the drum be now rotated to the right until the second line coincides with the spider wire, the wave-length reading should be 5890, and there should be no relative displacement of line and spider wire when the eye is moved in front of the eye-piece. If this is so, the spectrometer can be regarded as properly adjusted, and can then be used to determine the wave-lengths of other spectral lines. In measuring the wave-lengths of a series of lines, always set the spider wire first to the line of longest wave-length, because, on rotating the drum to the right, lines of shorter wave-length are brought into the field.

In using this instrument it has been found that there is a small error associated with the readings, the value of which depends on the wave-length. Thus we have :—

Wave-length in A. . .	4000	5000	6000	7000	8000
Error in A.	1	1	1·6	3	5

[1] The accurate adjustment to coincidence is secured by moving the spider wire in the telescope by means of the small screw at the side of the eye-piece.

Balmer's Series.—By means of the wave-length spectrometer, measure the wave-length of as many as possible of the lines of the hydrogen spectrum, and compare the values obtained with those calculated from the expression : $\lambda = 3645 \cdot 6\left(\dfrac{m^2}{m^2 - 4}\right)$, where m is successively given the values of 3, 4, 5, etc.

Absorption Spectra.—Coloured substances owe their colour to the fact that they selectively absorb rays or groups of rays of definite wave-length. When white light is passed through a coloured substance, the spectrum will no longer be continuous, but will show one or more dark bands, the position of which is characteristic of the particular substance.

EXPERIMENT.—*Determination of the Absorption Spectrum of Solutions of Potassium Permanganate.*

Set up and adjust the wave-length spectrometer, as previously explained. In front of the slit place a rectangular cell with parallel, plane glass sides, which may be, say, 1 cm. apart. Fill this cell with a 0·05-N solution of potassium permanganate (1·58 g. $KMnO_4$ per litre), and pass through it light from a 60-watt electric light bulb with frosted glass. Determine the wave-lengths of the edges of the absorption bands. Similar determinations are then made with solutions of one-half, one-quarter, one-eighth, etc., of the original concentration, the dilution being continued until the spectrum becomes practically continuous.

Represent the results obtained on a graph in which the logarithms of the concentrations are plotted against the wave-lengths of the edges of the absorption bands.[1]

Additional Experiments.—Investigate the absorption spectra of violet and green solutions of chrome alum. Prepare a violet solution of chrome alum by dissolving 10–15 g. of the salt in 100 ml. of *cold* water. The absorption cell should have walls about 4 cm. apart.[2] Examine the absorption spectra at different dilutions. The violet solution is then heated so as to convert the violet to the green salt. Examine, as before, the absorption spectra of the green solution. Investigate, also, the absorption spectra of cobalt chloride dissolved (*a*) in water, and (*b*) in ethyl alcohol.

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[1] The comparison of absorption spectra is rendered very convenient by using a spectrograph in which the telescope is replaced by a photographic camera. A series of spectra can be photographed on one plate. A panchromatic plate must be used.

[2] Otherwise a more or less concentrated solution must be used.

B. Refractometric Measurements

Refractive Index.—When a ray of monochromatic light passes from a less dense to a more dense medium, it is bent or refracted towards the normal. Thus, in Fig. 50, if I is the less dense and II the more dense medium, a ray of light passing from I to II will be bent so that the angle of refraction e will be less than the angle of incidence i; and, according to the law of refraction, the relation between these two angles will be such that—

$$\frac{\sin i}{\sin e} = \frac{N}{n}$$

where n is the index of refraction of the less dense, and N the index of refraction of the more dense medium. As the angle i increases, the angle e also increases, and reaches its maximum value when i becomes equal to a right angle; that is, when the incident light is horizontal. Since $\sin 90° = 1$, the above equation becomes $1/\sin e = N/n$, or $\sin e = n/N$.
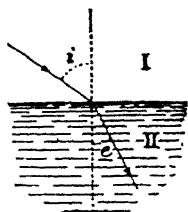
The methods to be described here of determining the refractive index of a liquid are based on the law of refraction just stated.

FIG. 50.

Specific and Molecular Refractivity.—Whereas the refractive index of a substance varies with the temperature, it was found (Gladstone and Dale) that the expression $\frac{n-1}{d}$, where d is the density, remains nearly constant at different temperatures. Still more is this the case with the expression $\frac{n^2-1}{n^2+2} \cdot \frac{1}{d}$ (Lorentz and Lorenz). The value of these expressions is, therefore, dependent only on the nature of the substance, and is a characteristic of it. It is called the *specific refractive power* or *refractivity* of the substance. If the value of the refractivity is multiplied by the molecular weight of the substance, one obtains the *molecular refractivity*. The latter is, therefore, equal to $\frac{M(n-1)}{d}$, or to $\frac{n^2-1}{n^2+2} \cdot \frac{M}{d}$, where M is the molecular weight.

Monochromatic Light.—Since the value of the refractive index varies with the wave-length of the light, it is necessary, in carrying out these measurements, to employ monochromatic light of definite wave-length. Formerly, light corresponding to the C, D, F and G' lines of the sun's spectrum was used as standard, but, in recent years, it has become customary to use other spectral lines, because of their superior spectral purity and of the greater brilliancy of illumination with which they can be produced. As light sources one may use those described on pp. 95–97. In the case of the light emitted by the sodium flame or sodium discharge lamp, the light may be rendered more truly monochromatic by passage through a dichromate solution or other suitable light filter.

On account of the great brilliance of the yellow and green mercury lines, it may be necessary, when making the reading for the violet mercury line, 4047 A., to interpose a piece of cobalt glass, or special light filter, in the path of the light from the mercury lamp.
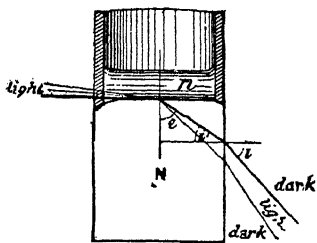
FIG. 51.

Determination of the Refractive Index of a Liquid by the Pulfrich Refractometer.—The liquid, the refractive index of which is to be determined, is placed in a cell cemented to the top of a right-angled glass prism (Fig. 51), the refractive index of which must be known, and must be greater than that of the liquid. A beam of monochromatic light entering the liquid will be refracted through the prism in the manner shown in the figure. If one considers the path of the last ray to enter the prism, namely, the horizontal ray (represented by the thick line), then $\sin e = n/N$, where n is the index of refraction of the liquid, and N that of the glass (referred to that of air equal to unity). Further, $\sin i/\sin i' = N$. But $\sin e = \cos i'$, and therefore $n = N \cos i'$. But $\cos^2 i' = 1 - \sin^2 i'$; hence $n = N\sqrt{1 - \sin^2 i'}$. Substituting for $\sin^2 i'$ the value $\sin^2 i/N^2$ one obtains $n = \sqrt{N^2 - \sin^2 i}$.

If, therefore, the value of N (the refractive index of the glass), and the angle i at which the light emerges from the prism are known, the value of n, the refractive index of the liquid, can be calculated. A table of values of $\sqrt{N^2 - \sin^2 i}$

for the particular prism and for different values of i is supplied by the makers.

Regulation of the Temperature.—As the density, both of the prism and of the liquid under investigation, alters with temperature, it is necessary, in measurements of any considerable degree of accuracy, to be able to maintain the prism and the liquid at constant temperature. In the form of Pulfrich refractometer described below, this is effected by means of the arrangement shown in Fig. 52. The prism is surrounded by a metal box, L, through which water circulates. After passing round the prism, the water is led, by means of a rubber tube, into the heating tube S, which is lowered into the liquid in the cell, and then passes to the waste. A thermometer screwed into the heating tube S shows the temperature of the circulating water, and must be fixed into position before water is passed through the heater.
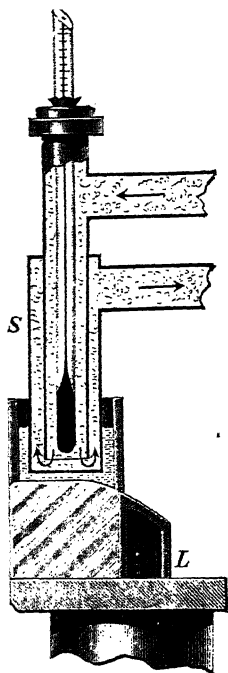
Pulfrich Refractometer.—The Pulfrich refractometer (as made by Zeiss) is shown in Fig. 53, the instrument being viewed from the back in order to show the optical parts. This instrument is arranged for illumination either by a coloured flame or by means of a Plücker tube (Q).[1]

FIG. 52.

Place the refractometer on a table sufficiently broad to allow of a sodium flame being placed about 20 inches away from the instrument, and opposite to the reflecting prism N, which is arranged to swing outwards or inwards. The refracting prism (L), carrying its glass cell,[2] is first of all placed

[1] Improved forms of the Pulfrich Refractometer are now produced by Adam Hilger, Ltd., 75A, Camden Road, London, N.W.1, and by Bellingham and Stanley, Ltd., 71, Hornsey Rise, London, N.19. Besides improvements in mechanical design, a more efficient waterjacket has been provided both for the prism block and for the cell. The manipulation of these instruments is essentially the same as for the Zeiss pattern. With these refractometers, tables for the lithium, mercury, and cadmium lines (see p. 99), as well as for the sodium and hydrogen lines, are supplied.

[2] The glass cell may be cemented to the prism by means of fish-glue or seccotine, the cement being applied in a thin uniform layer to the edge of

in position on the triangular standard ; the prism being allowed to sink as far as it will go, and then fixed by means
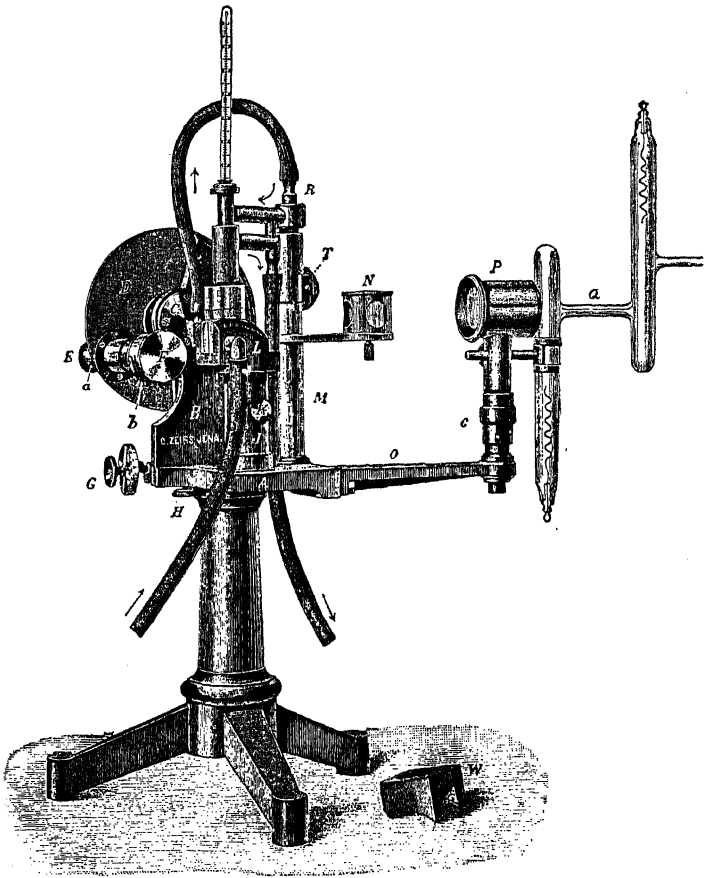
FIG. 53.

of the screw K.[1] The flat face of the prism must, of course,

the glass cylinder.   This is facilitated by means of a glass block, the surface of which is ground so as to have the same curvature as that of the edge of the cylinder.   The cement is first rubbed on the surface of the block, and the edge of the cylinder then placed on the block and carefully turned round so as to apply a thin coating of cement.

When the temperature of the experiment is not high, the cell may frequently be attached to the cylinder by means of vaseline.   In this case, however, it is very easily displaced.

[1] In this, as in all such cases, only a very gentle pressure must be exercised in tightening the screw.

point towards the telescope tube F. The rubber tube attached to the heater (at R) is placed in position over the conical connecting piece in the side of the prism case, and the thermometer screwed into the top of the heater. Water from a thermostat can then be caused to circulate round the prism and through the heater (S), the water being passed in at L, and allowed to run to the waste through the tube connected with the heater.

The light, after refraction through the prism, passes into the telescope tube through an elongated oblong slit in the cap F. This can be rotated through a certain angle, but there are four points at which it is fixed by stops, the action of which will be felt on rotating the cap. In one position the whole of the oblong slit is open to the prism, in two other positions only half the slit is open, while in the fourth position the aperture is closed altogether. The half-slits are used only when observations are being made with a divided cell ; when a single cell is used, the whole slit must be open.

On examining the face of the disc D, to which the telescope is attached, it will be seen that it is graduated over a quarter of its circumference into degrees and half-degrees (30') ; and there is a vernier with thirty divisions, by means of which single minutes can be read. The reading of the vernier is facilitated by a small lens, which can be moved in front of the scale. For the purpose of making fine adjustments, the disc is fixed by means of the screw H, and the fine adjustment made by means of the screw G.

When it is desired to use a Plücker tube as the source of illumination, the latter (Q) is clamped to the standard c, so that the end of the capillary is opposite the middle of the lens P, whereby the light is focussed on the cell.[1]

Determination of the Zero Point.—Before proceeding to make a measurement, the correction for zero, if any, must first be ascertained. This is done with the help of a small

[1] In more recent forms of the apparatus, the upright standard is replaced by a curved arm carrying both the lens P and the Plücker tube ; and this arm can be moved upwards or downwards so that the angle at which the light enters the cell can be altered slightly. In this way, one can correct for slight displacements of the cell-walls from the perpendicular, and also their want of parallelism with the face of the prism, and so obtain sharper and clearer lines. This newer form of attachment also is furnished with a screw which allows of the Plücker tube being moved laterally ; and with a metal diaphragm which allows one to cut off some of the light passing through the lens, and so sharpen the spectrum lines in the field of view.

right-angled prism, *a*, let into the side of the telescope tube near the eye-piece. The disc is first of all rotated until its zero coincides approximately with the zero of the vernier, and is fixed in this position by means of the screw H. A source of illumination (best, a small electric lamp or " torch ") is then fixed opposite to the prism *a*. On looking through the eye-piece of the telescope, the field of view will have the appearance shown in Fig. 54. To the right is seen the prism *a*, while to the left of the field of view is seen a bright rectangular patch, *a'*, crossed by two lines running parallel to the cross-wires *w*. This bright patch is the image of the prism *a* reflected from the face of the refracting prism (L), and the two marks are the images of the cross-wires. The zero of the instrument is given when the cross-wires *w* coincide with their images. The adjustment to coincidence is carried out by means of the fine adjustment screw G, and the point on the scale opposite to the zero of the vernier is then read. This is the zero of the instrument, and the difference of this reading from the zero mark is the correction which has to be applied to each subsequent reading of the scale.
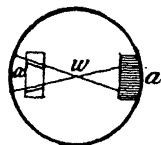
FIG. 54.

It happens, however, not infrequently, that the prism L is slightly turned in its bed, so that the image of the prism and cross-wires is thrown either nearer to or farther from the centre of the field of view. In this case, simultaneous coincidence of both the cross-wires with their images cannot be obtained. The zero is, in such a case, determined by setting the upper cross-wire in coincidence with the upper image, then the lower cross-wire in coincidence with the lower image, and taking the mean of the two readings.

Having ascertained the zero correction, we may now proceed to make measurements of the refractive index.

EXPERIMENT.—*Determine the Refractive Index of Acetone for the D Line.*

The refractometer is set up as described above, a sodium flame being used as source of illumination. This flame is placed at a distance of 18 to 20 inches from the reflecting prism N, which must be swung into position so as to throw an image of the flame on the side of the cell on the top of the prism L. (The arm carrying the reflecting prism should be swung as far as it will go towards the back of the instru-

ment.) In order to exclude extraneous light, and also to diminish fluctuations of temperature, a black wooden cap, W (Fig. 53), is placed over the cell. In one side of this cap a notch is cut, through which the light enters into the liquid in the cell.

Place a small quantity of acetone in the cell so as to form a layer about 4 mm. deep. Swing the heating tubes into place, and lower the heater S (the outside of which must be quite clean) into the cell by means of the milled head T (Fig. 53) ; a stop prevents the heater from being lowered too far. Lower the movable flange on the heater until it is in contact with the top of the cell. Circulate water from a thermostat (p. 42) round the prism and through the heater, the temperature of the water being regulated to, say, 25°. Make sure that the acetone does not evaporate entirely in the course of the measurements.

When the temperature has become constant (within 0·1°), loosen the screw H, and rotate the disc until the refracted beam of light is visible, forming a band of yellow light across the field of view. Fix the disc, and then, by means of G, place the intersection of the cross-wires on the *upper* sharp edge of the yellow band, the cross-wires having first been focussed sharply by rotating the eye-piece.

Make several determinations of the point of coincidence, and take the mean as the correct value. The individual readings should not differ from the mean by more than one minute.

Having in this way determined the angle of emergence, the index of refraction can be obtained from the tables supplied by the makers of the instrument.

To illustrate the use of the table, the following example may be taken :—

Suppose the angle of emergence to be 64° 45′. On looking up the tables for the particular prism (Ia), we find the following numbers—

i	n_D	Δ_n	Correction values for—		
			C	F	G′
64° 30′ 40′ 50′ 65° 0′	1·34647 564 480 1·34397	8·3 8·4 8·3	588 8 9 589	1475 6 7 1478	2729 31 3 2735

Under the heading i are the angles of emergence read ; under n_D, the refractive index of the liquid, calculated according to the equation $n = \sqrt{N^2 - \sin^2 i}$. The numbers under $\varDelta_n$ are the differences in units of the last decimal place of the value of the refractive index for a difference of $1'$ in the value of the angle of emergence. The last three columns of the table will be explained later.

The angle of emergence with sodium light (D line of sun's spectrum) we have supposed to be $64° \ 45'$. The value of n_D for $64° \ 40'$ is $1·34564$, and the difference in the value of n for $1'$ is $8·4$; so that the value of n_D for the angle $64° \ 45'$ will be $1·34564 - 0·00042$ $= 1·34522$.

Having obtained the value of the refractive index from the tables, and the density of the liquid at the temperature of the experiment having been determined (p. 62), the specific and molecular refractivities can be calculated by means of the formulæ—

$$r_L = \frac{n^2 - 1}{n^2 + 2} \cdot \frac{1}{d}, \qquad \text{and} \qquad [R]_L = \frac{n^2 - 1}{n^2 + 2} \cdot \frac{M}{d}$$

r_L here represents the refractivity calculated according to the formula of Lorentz and Lorenz, involving the square of the refractive index, in order to distinguish it from r_G, the refractivity according to the formula of Gladstone and Dale, $(n-1)/d$.

The value of $[R]_L$ obtained, should be compared with the value calculated from the sum of the atomic refractivities. Some of these values, for the spectrum lines C, D, F and G', are given in the following table [1] :—

VALUES OF ATOMIC REFRACTIVITIES FOR SOME OF THE ELEMENTS, CALCU-
LATED ACCORDING TO THE r_L FORMULA.

Element.	Symbol.	r_C	r_D	r_F	r_G
Carbon (singly bound) .	C'	2·413	2·418	2·438	2·466
Hydrogen	H	1·092	1·100	1·115	1·122
Oxygen (in OH group) .	O'	1·522	1·525	1·531	1·541
,, (in ethers) . .	O‹	1·639	1·643	1·649	1·662
,, (in CO group) .	O''	2·189	2·211	2·247	2·267
Chlorine	Cl	5·933	5·967	6·043	6·101
Bromine	Br	8·803	8·865	8·999	9·152
Iodine	I	13·757	13·900	14·224	14·521
Ethylene bond . . .	⊨	1·686	1·733	1·824	1·893
Acetylene ,, . . .	⫤	2·328	2·398	2·506	2·538

[1] See Eisenlohr, *Z. physikal. Chem.*, 1911, **75**, 585, or Roth and Eisen-
lohr, *Refraktometrisches Hand- und Hilfsbuch.*

In the preceding table—

r_C denotes the atomic refractivity for the C (or H_α) line (red) of the hydrogen spectrum ;

r_D denotes the atomic refractivity for the D line (sodium light) ;

r_F ,,   ,,   ,,   ,,   F (or H_β) line (blue) of the hydrogen spectrum ;

r_G denotes the atomic refractivity for the G′ (or H_γ) line (violet) of the hydrogen spectrum.

When a measurement has been completed, as much as possible of the liquid is withdrawn from the cell by means of a pipette, the point of which *must be placed against the lower junction of cell and prism*, and must not be allowed to touch the upper polished surface of the prism, which might thereby be scratched. The last traces of liquid are removed by means of filter paper.

Correction for Temperature.—The values of the refractive index given above (p. 110) refer, strictly, only to the temperature of 20°. When measurements are made at any other temperature, a correction has to be applied. Tables of temperature corrections for the different prisms are issued by the instrument makers. To illustrate the use of the tables, we may take the table for Prism I, supplied by Zeiss with their Pulfrich refractometer :—

TABLE OF TEMPERATURE CORRECTIONS.

n	Correction in units of the fifth decimal place of n.		
	C	D	G′
1·60	0·25	0·29	0·52
1·50	0·26	0·30	0·55
1·40	0·28	0·33	0·59
1·30	0·30	0·35	0·64

To make the temperature correction, look up the value of the correction for the different spectrum lines to be applied to values of n of the order given in the first column ; multiply this number by the temperature difference $(t-20)$, where t is the temperature at which the measurements were made, and add the result (units of the fifth decimal place) to the value of n taken from the tables.

Thus, suppose a determination to have been carried out at 30°, and the angle 64° 30′ obtained as the angle of emergence, with Prism I using the D line. From the table on p. 110 we see that $n_D = 1·34647$ at 20°. The value of the correction is,

from the preceding table, $0·35 \times (30-20) = 3·5$. This must be added to the fifth place in the above value of n, and we obtain $1·34651$.

EXPERIMENT.—*Determine the Refractive Index of Acetone for the C, F, and G' lines of the Hydrogen Spectrum.*

A Plücker hydrogen tube is clamped in position as already described (p. 108), so that the light is focussed at the notch of the wooden cap of the cell, the reflecting prism N (Fig. 53) being pulled forward out of the path of the light. After having placed a quantity of acetone in the cell, the position of the tube must be adjusted so that, on looking through the telescope, the lines appear at their brightest and are most clearly defined. The adjustment is best carried out by first roughly adjusting the position of the tube, while in action, by hand, and then moving the tube and lens upwards or downwards, or the tube sidewise by means of the different adjusting screws, until the best position is obtained. After the lines have been obtained quite clear and bright, they may be narrowed down and sharpened somewhat by means of the movable diaphragm in front of the lens.

The chief lines of the hydrogen spectrum which one sees are a bright red line on the extreme right (C line), a pale blue line (F line), and, on the extreme left, two violet lines (G' and G'').[1]

The temperature having been regulated as described on p. 106, the Plücker tube is put in action, and the angle of emergence for the C line determined by bringing the intersection of the cross-wires into coincidence with the upper edge of the red line. After reading the angle on the graduated disc, the latter is turned by means of the fine-adjustment screw G (Fig. 40) until the cross coincides with the upper edge of the violet line, G', when the angle is again read.

Instead of reading the angle of emergence for each line on the scale of the disc, it is only necessary to do so for one of the lines, the position of which is determined accurately. The position of the other lines is then determined by difference by means of the scale on the drum-head of the micrometer screw G. This drum is graduated into 200 parts, and moves in

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[1] Owing to differences in the relative dispersive power of the prism and the liquid, the order of the lines may not in all cases be that given above. The measurements and calculations are, however, thereby in no way interfered with.

8

front of a horizontal scale, graduated into divisions corre-
sponding to degrees and thirds of a degree (20'). One com-
plete turn of the micrometer screw causes the drum to
advance or retreat across one of the subdivisions of the
horizontal scale, and the telescope to move through an angle
of 20'. Consequently, as there are 200 divisions on the drum,
each of these is equivalent to 0·1'. The use of the graduated
drum is especially advantageous for the determination of the
angle of dispersion of a substance ; and the only precaution
that requires to be observed in its use is to turn it always
in the same direction when bringing the cross-wires of the
telescope into coincidence with the boundary-line of light.

Having obtained the value of the angles of emergence for
the C, F, and G' lines, the value of the refractive index is
obtained from the tables (p. 110), the numbers in the columns
C, F, G' giving the numbers (in units of the fifth decimal
place) which must be subtracted from or added to the value
of n_D in order to give the value of the refractive index for the
other lines. In the case of the C line, the correction value
must be subtracted from the value n_D ; in the case of the F
and G' lines, the correction value must be added. Thus,
suppose the angles read were 64° 30' and 65° 0' for the C and
G' lines respectively, then from the tables we obtain—

$$n_C = 1·34647 - 0·00588 = 1·34059$$
$$n_G = 1·34397 + 0·02735 = 1·37132$$

From the values of the refractive index, the molecular
refractivity for the C, F, and G' lines should be calculated,
and also the value of the molecular dispersivity (the differ-
ence of the molecular refractivities) between the C and F
lines ; and the numbers compared with the sum of the
atomic refractivities given on p. 111.[1]

**Determination of the Refractive Index of a Liquid by the
Abbe Refractometer.**—In the Abbe refractometer there is a
fixed telescope and the liquid under investigation is placed
in contact with the hypotenuse face AB (Fig. 55) of a right-
angled prism ABC. From the theory of refraction, a ray of
monochromatic light passing through the liquid and entering
the prism at grazing incidence, will emerge from the face AC
along a path perpendicular to that face, provided $n = N \sin A$.

[1] For the values of the refractive index, the molecular refractivity, and
the molecular dispersivity of a large number of substances, see Eisenlohr,
Z. physikal. Chem., 1911, **75**, 585.

For any other value of n, however, the ray of light will emerge at an angle to the face AC, less than a right angle, and in order that the ray may be brought parallel with the axis of the telescope, T, the prism must be rotated through a certain angle a. By determining the value of the angle
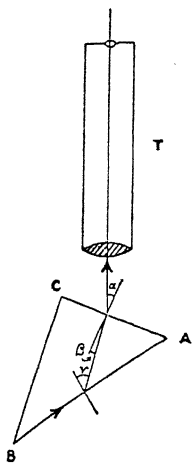
FIG. 55.
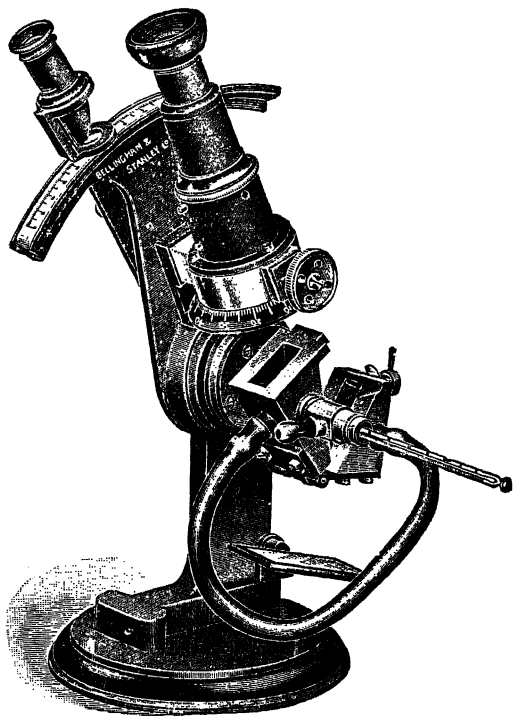
FIG. 56.

of emergence, a, the refractive index of the liquid, n, can be calculated from the relations: $N = \dfrac{\sin a}{\sin \beta}$; $\beta + r = A$; $n = N \sin r$. By eliminating β and r, we obtain—

$$n = \sin A \sqrt{N^2 - \sin^2 a} - \cos A \sin a$$

The Abbe Refractometer.—This instrument, shown in Fig. 56, possesses several advantages over the Pulfrich refractometer in that on it the refractive index, n_D, is read directly with an accuracy of about 0·0002, only a few drops

of liquid are required for examination, and either mono-chromatic light or white light can be used.

In order to carry out a determination of the refractive index of a liquid, open the prism box and place a few drops of the liquid on the ground surface of the lower prism. Close and fasten the prism box again, taking care (by tilting the refractometer forward a little, if necessary) that the liquid does not flow away. A film of liquid will thus be enclosed between the two prisms. Focus the cross-wires of the telescope by rotating the eye-piece and adjust the mirror so as to give a good illumination. By means of the arm at the side of the apparatus, turn the prism box slowly backwards and forwards until the field of view becomes partly light and partly dark. When white light is used the edge of the light band will show a coloured fringe. By means of the milled screw-head on the telescope, rotate the " compensator " (consisting of two prisms, which rotate in opposite directions, and so form a system of variable dispersion) until the coloured fringe disappears and the light-band shows a sharp edge. Now rotate the prism box until this sharp edge is in coincidence with the intersection of the cross-wires in the telescope, and read off directly the index of refraction on the divided arc, by means of the magnifying lens. This lens should be turned so that the inner reflecting surface of the tube illuminates the scale. The third decimal place in the refractive index can be read directly, and the fourth can be estimated with an accuracy of about $\pm 0 \cdot 0002$.

For the purposes of temperature regulation, the prisms are enclosed in a metal jacket through which water can be circulated. Before circulating the water, the thermometer must be screwed into place.

The readings on the divided arc give the value of the refractive index for the D line (n_D). Connected with the compensator, however, there is a divided circle, and by reading the number on this dispersion circle after the light-band in the telescope has been made sharp and free from colour fringe, the value of the dispersion, $n_F - n_C$, can be calculated from tables supplied with the instrument.

Adjustment of the Refractometer.—It may, from time to time, be necessary to adjust the setting of the refractometer, and for this purpose a standard glass test-piece is provided, the index of refraction of which is marked on the glass. Open the prism box until the lower prism can be slipped off its hinge. By means of a drop of monobromnaphthalene applied to the polished surface of the test-

piece, fix the latter on the surface of the upper prism, the ground edge of the test-piece being directed towards the mirror. Excess of the monobromnaphthalene is to be avoided. Turn the lever so that the reading on the divided arc corresponds with the refractive index of the glass test-piece, and by means of the compensator obtain a sharp band of light, without colour fringe, in the telescope. If this edge coincides with the intersection of the cross-wires, then the instrument is in proper adjustment ; but if not, turn the small, square-cut pin at the back of the telescope by means of the special key, until coincidence occurs.

The Immersion Refractometer.—When comparatively large quantities of material are available, the dipping or immersion refractometer may be used. In this instrument, the optical principle of which is the same as that of the Abbe refractometer (Fig. 55), the prism is rigidly fixed in the telescope tube, in which also there are contained a compensating prism (as in the Abbe apparatus) and a scale. In use, the refractometer is suspended so that the prism dips into the liquid to be investigated, which is contained in a beaker immersed in a thermostat, regulated to a temperature of 17·5°, the temperature for which the instrument is calibrated. White light is reflected by means of a mirror placed below the beaker, and the sharp edge of the band of light is read off on the scale. In order that fractions of a scale division may be determined with greater accuracy, there is a fine adjustment screw, with graduated drum, by means of which the scale can be moved. At the beginning of the determination, this micrometer screw should be placed in the zero position, and if the edge of the light-band does not coincide with a scale division, the drum is rotated until coincidence occurs. From the graduation on the drum, the fraction of a division through which the scale has been moved can be read off. The position of the edge of the light-band having been determined, the scale reading can be converted to refractive index value by means of the table provided with the instrument. The refractive indices are for the D (sodium) line. The prism usually supplied is suitable chiefly for aqueous solutions with a refractive index between, say, 1·325 and 1·366. Interchangeable prisms, however, are also made so that the range of refractive indices for which the instrument can be used is extended.

Before use, the adjustment of the instrument must first be tested with water at 17·5°. If the edge of the light-band does not coincide with the scale division appropriate to the

prism used, the scale must be moved until coincidence is obtained. The reading on the micrometer screw drum then gives the correction which must be applied to each scale reading in order to give the correct value of the refractive index.

Refractometric Determination of the Composition of Solutions.—Refractometric measurements may be used, very advantageously, for the quantitative determination of the composition of binary solutions. For this purpose, the refractive indices of a series of solutions of known composition are first determined (*e.g.* by means of the Abbe or immersion refractometer), and the values so obtained are plotted in a graph. The composition of an unknown solution can then be ascertained from the graph after the index of refraction of the solution has been determined.[1]

The composition of a *dilute* solution of two liquids can be calculated approximately from the refractive index of the solution, provided one knows the refractive indices and densities of the two components. If n_1 and n_2 are the refractive indices of the two components, and n_3 the refractive index of the solution, and if d_1, d_2, and d_3 are the corresponding densities, the percentage amount, p, of component I can be approximately calculated by means of the expression,

$$\frac{n_1 - 1}{d_1} \cdot p = 100 \cdot \frac{n_3 - 1}{d_3} - \frac{n_2 - 1}{d_2} \cdot (100 - p)$$

The refractive index of a solution, calculated by means of this expression, should be compared with that determined directly.

C.—Polarimetric Measurements

When ordinary light is passed through a Nicol's prism (made from Iceland spar), the emergent ether vibrations take place in one plane, and the light is said to be plane-polarized. If this polarized light is now examined by means of another Nicol's prism, it will be found that, on rotating the latter, the field of view appears alternately light and dark, the minimum of brightness following the maximum as the prism is rotated through an angle of 90°. The prism by which the light is polarized is called the *polarizer*, and the

[1] The relation between refractive index and composition in the case of a large number of solutions is given in the " Tables " prepared by R. Wagner for use with the immersion refractometer.

second prism, by which the light is examined, is called the *analyzer*.

If, when the field of view appears dark (which occurs when the axes of the two prisms are at right angles to each other), a tube containing a solution of cane sugar is placed between the two prisms, the field lights up ; and one of the prisms must be turned through a certain angle, a, before the field becomes dark again. The solution of cane sugar has therefore the power of turning or rotating the plane of polarized light through a certain angle, and is hence said to be optically active. When, in order to obtain darkness, the analyser has to be turned to the right, *i.e.* clockwise, the optically active substance is said to be *dextro-rotatory*; and *lævo-rotatory* when the analyser must be turned to the left.

It will, of course, be possible to obtain a position in which the field of view becomes dark by rotation of the analyser either to the right or the left, because in one complete rotation of the prism through 360°, there are two positions of the analyser, 180° apart, at which the field is dark, and similarly, two positions at which there is a maximum of brightness. In determining the sign of the activity of a substance, one takes the direction in which the rotation required to give extinction is less than 90°.[1]

The angle of rotation depends on (1) the nature of the substance, (2) the length of the layer through which the light passes, (3) the wave-length of the light employed (the shorter the wave-length, the greater the angle of rotation), (4) the temperature. In order, therefore, to obtain a measure of the rotatory power of a substance, these factors must be taken into account, and one then obtains what is known as the *specific rotation*. This is defined as the angle of rotation produced by a liquid which in the volume of 1 ml. contains 1 g. of active substance, when the length of the column through which the light passes is 1 dcm. The specific rotation is represented by $[a]$, the observed angle of rotation being represented simply by a.

When, therefore, one is dealing with an homogeneous active liquid, the specific rotation is represented by—

$$[a] = \frac{a}{l \cdot d}$$

[1] This, however, is not a universal rule. See Landolt, "Das optische Drehungsvermögen."

where l is the length of the column of liquid in decimetres, and d is the density. If, further, account is taken of the other factors on which the rotation depends, viz. temperature and wave-length of light, one obtains a number which, for the particular conditions of experiment, is a constant, characteristic of the substance. Thus, $[\alpha]_D^{25°}$ represents the specific rotation for the D line (sodium light) at the temperature of 25°.

When the active substance is examined in solution, the concentration must be taken into account, in accordance with the expressions :

$$[\alpha]=\frac{100 \cdot \alpha}{l \cdot c} \text{ or } [\alpha]=\frac{100 \cdot \alpha}{l \cdot p \cdot d}$$

where c is the number of grams of active substance in 100 ml. of solution, p is the number of grams of active substance in 100 g. of solution, and d is the density of the solution. In expressing the specific rotation of a substance in solution, the concentration and the solvent (which also has an influence on the rotation) must be stated.

Apparatus.—*The Polarimeter.*—The arrangement of the optical parts of the Lippich polarimeter, the type now generally adopted, is shown diagrammatically in Fig. 57.
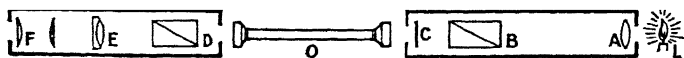
FIG. 57.

Monochromatic light from the source L passes through the lens A, which renders the rays of light parallel, and then through the polarizing prism B. It then passes through the observation tube O, and thence through the analyser D. The field of view is observed through the telescope EF. At C there is a small Nicol prism which covers half of the opening at the end of the polarizer tube. The light on passing through this prism is altered in phase by half a wave-length, but still remains plane-polarized. In this way, two beams of polarized light are obtained ; and if the polarizer is rotated so that the plane of polarization forms an angle (δ) with the optical axis of the Nicol prism, the planes of polarization will also be inclined at an angle, equal to 2δ. This is the half-shadow angle. On rotating the analyser, a position will be found at which the one beam will be completely, the

other only partially, extinguished. The one half of the field of view, therefore, will appear dark, while the other half will still remain light (as shown by C'). On rotating the analyser still further, through the angle 2δ, a second position will be found at which the second beam will be extinguished, while the first is no longer so. In this position of the analyser, the half of the field which was formerly bright will now be dark, and that formerly dark will now be light. When, however, the analyser occupies an intermediate position, the field of view will appear of uniform brightness; and this is the position to which the analyser must be set.

By diminishing the angle δ (by rotating the polarizer), the sensitiveness of the instrument can be increased, because now the angle 2δ, through which the analyser must be rotated in order to cause the shadow to pass from one half to the other of the field of view, is diminished. By diminishing the angle of half-shadow, however, the uniform illumination of the field of view is also diminished, so that the increased sensitiveness due to diminution of the angle of half-shadow is partly counteracted by the greater difficulty in deciding when the field is uniformly illuminated, unless the light intensity of the source can at the same time be increased. With a source of light of given intensity, therefore, the angle of the half-shadow must be fixed so that the determination of the position of uniform illumination can be made without unduly straining the eyesight.

The complete polarimeter is shown in Fig. 58.

At the end S, which is directed towards the source of light, are the lens and the light-filter, consisting either of a solution of potassium dichromate or of a crystal of this salt. The polarizing prism is at P, and is connected with the lever h, by means of which it can be rotated, and thus the angle of half-shadow altered. The observation tube is placed in the middle part of the instrument, and is protected from extraneous light by a cover. The analyser is placed in the portion of the tube at A, and can be rotated, independently of the graduated circle, by means of a screw. This allows of the correction of the zero point. F is the telescope with eye-piece. K is a graduated disc, which can be caused to rotate, along with the analyser and telescope, past the fixed verniers n and n' by means of the rack and pinion T.[1] By

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[1] Various arrangements are employed for rotating the analyser, and the better instruments are also fitted with a fine adjustment.

means of the two movable magnifying lenses *l*, the accuracy
of the reading is increased.

Source of Illumination.—As has already been said, the
angle of rotation depends on the wave-length of the light
used. It is therefore necessary to employ monochromatic
light. On account of the ease with which the yellow light of
incandescent sodium vapour (corresponding with the D line
of the solar spectrum) can be obtained (p. 96), polarimetric
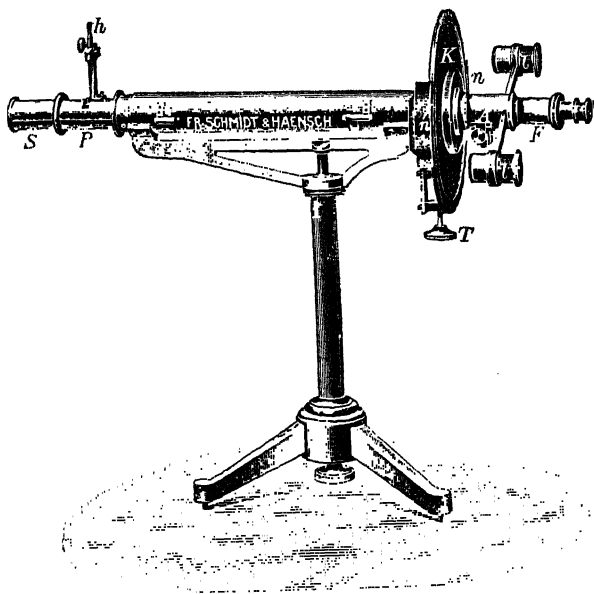
FIG. 58.

measurements are very frequently carried out with this
light.

The light given by a sodium flame or electric discharge
lamp is not spectroscopically homogeneous, and for accurate
measurements the light should be purified by passage
through an orange solution of potassium dichromate and a
green solution of uranous sulphate.

Measurements of the angle of rotation for the yellow,
green, and violet lines of the mercury spectrum (p. 99) are
now frequently made. For this purpose, a spectroscopic
arrangement, consisting of a constant deviation prism
(p. 100), and a lens which projects an image of the light

source on the prism of the polarizer, is attached to the end of the polarimeter. An electric lamp of high candle-power serves as the source of light.[1]

Observation Tubes.—The observation tube in which the liquid to be examined is placed, generally consists of a tube of thick glass with accurately ground ends. The tube is closed by means of circular plates of glass with parallel sides, which are pressed against the ends of the tube by means of screw-caps (Fig. 59). These caps must not be screwed so tightly that they strain the glass plates. Since the unit of length in polarimetry is 1 dcm., these tubes are made equal to 1 dcm. or to some multiple, *e.g.* 2 or 4 dcm., or a fraction, *e.g.* 0·5 dcm.

For the maintenance of a constant temperature, tubes are also made surrounded by a metal jacket, through which water

FIG. 59.

at constant temperature can be circulated by means of a pump (p. 42).

Adjustment of the Polarimeter.—Set up the polarimeter so that the polarizer end is opposite to a bright sodium flame or electric discharge lamp, which is placed at a distance equal to the focal length of the lens at the end of the polarimeter. Place a tube full of distilled water in the support between the polarizer and the analyser, and focus the telescope eye-piece on the line bisecting the field of view, rotating the analyser if necessary so as to get unequal illumination of the two halves. Now determine the zero point by rotating the analyser until equal illumination of both halves of the field of view is obtained. This position should be approached several times from either side, readings being made at each of the two verniers (in instruments supplied with these), and the mean of the readings taken. The object of making readings at the two verniers, *i.e.* at points of the graduated circle about 180° apart, is to correct for the eccentricity of the latter.

As the zero is altered by alteration of the angle of half-shadow, the position of the lever *h*, which rotates the

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[1] A purer monochromatic light can be obtained by using a mercury vapour lamp and purifying the light by means of a direct vision prism.

polarizer, must be fixed before the zero point is determined. In some instruments it is possible to rotate the analyser without rotating the graduated circle (or the vernier where the latter is movable), and it is therefore possible to adjust the zero so as to eliminate the correction for the zero point. Further, it is possible by this means to adjust the zero to different parts of the graduated scale, and thus eliminate errors in graduation.

EXPERIMENT.—*Determine the Specific Rotation of Cane Sugar.*

Make up a solution of pure cane sugar in distilled water of known concentration. This can be done either by weighing out the sugar, previously dried in a steam oven, dissolving in water, and making the solution up to a definite volume (say, 100 ml.) in an accurate measuring flask ; or by weighing both the sugar and the solution, and determining the density of the latter by means of a pyknometer. The strength of the solution used may be about 10 per cent.

Having adjusted the polarimeter as described above and determined the zero point, the sugar solution, contained in an observation tube fitted with a water-jacket, is placed in the polarimeter, and the angle of rotation observed, several readings being taken as in the determination of the zero point. Meanwhile the temperature of the solution is maintained constant, equal say to 20°, by circulating water from a thermostat through the mantle. Having determined the value of the angle of rotation, the specific rotation is calculated by means of the formulæ on p. 120. The value of $[\alpha]_D^{20°}$ for cane sugar is $+66 \cdot 67° - 0 \cdot 0095c$, where c is the weight of the sugar in grams in 100 ml. of solution. Between the temperatures of 14° and 30°, $[\alpha]_D^t = +66 \cdot 67 - 0 \cdot 0247$ $(t-20)$.

CHAPTER VIII

OSMOTIC PROPERTIES OF SOLUTIONS. CALCULATION OF MOLECULAR WEIGHTS AND ACTIVITIES

THE osmotic pressure of a solution of moderate concentration is given by the well-known expression $P = \dfrac{RT}{V_0} \cdot \dfrac{n_2}{n_1 + n_2}$, where V_0 is the molecular volume of the solvent and $\dfrac{n_2}{n_1 + n_2}$ is the molar fraction of the solute. For very dilute solutions, this reduces to the van't Hoff expression $P = \dfrac{nRT}{V}$, where V is the volume of the solution, and n the number of gram-molecules of the solute. On the basis of the laws of osmotic pressure, therefore, and of the analogy between a substance in the gaseous state and in dilute solution, it is possible to calculate the molecular weight of a substance in solution from determinations of the osmotic pressure. Other properties of solutions, such as the lowering of the freezing-point, elevation of the boiling-point, and lowering of the vapour pressure, also depend on the concentration of the solution as expressed by the molar fraction of the solute, and these properties, therefore, are closely related to the osmotic pressure, and may be employed for the purpose of obtaining the value of the molecular weight and for studying changes in the molecular state of substances in solution. These properties are also of great value for the purpose of calculating what is known as the *activity* or "effective concentration" of a solute.

I. FREEZING-POINT (CRYOSCOPIC) METHOD

If w g. of a substance when dissolved in W g. of a solvent lower the freezing-point of the latter by $d°$, the molecular weight of the solute is obtained by means of the expression

$$M = K \frac{w}{dW}$$

where K is a constant depending only on the solvent. Its value for the commonest solvents employed is given in the following table :—

Solvent.	Freezing-point.	K.	Latent heat of fusion (cal.).
Acetic acid [1] . . .	$16 \cdot 6°$	3900	$44 \cdot 7$
Benzene	$5 \cdot 4°$	5120	$30 \cdot 4$
Water	$0°$	1858	$79 \cdot 7$
Nitrobenzene . .	$5 \cdot 72°$	6870	$22 \cdot 5$

The above expression is applicable only when the solute does not form an isomorphous mixture (solid solution) with the solid solvent, *i.e.* only when the solvent crystallizes out pure.
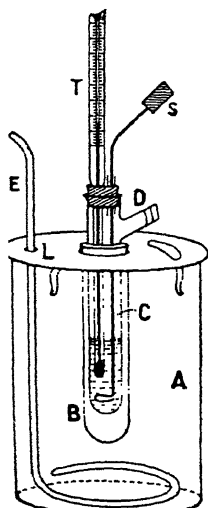
FIG. 60.

Apparatus.—In order to find the value of d in the above expression, it is necessary to determine the freezing-point of the pure solvent and of a solution of known concentration. This determination is carried out in the apparatus shown (Fig. 60).[2] The cooling bath consists of a glass or stoneware vessel, A, on the top of which rests a lid of brass, L. Through a hole in the centre of the lid there passes a wide glass tube, B, which is fixed in place by means of a cork ; and through another opening in the lid there passes a stirrer, E, by means of which the temperature of the bath can be kept more uniform. A third opening in the lid allows of the passage of a thermometer.

The freezing-point tube C, which is furnished with the side tube D, is supported in the neck of tube B by means of a cork or asbestos ring, so that the freezing-point tube is surrounded

[1] In the case of a hygroscopic solvent like acetic acid, special precautions must be taken to prevent access of moisture from the air. See, however, Roberts and Bury, *J. Chem. Soc.*, 1923, **123**, 2037.

[2] The method which is described here, and which is due essentially to Beckmann (*Z. physikal. Chem.*, 1888, **2**, 638 ; 1891, **7**, 323 ; 1894, **15**, 656 ; 1896, **21**, 239 ; 1903, **44**, 183), is that which is most commonly used in chemical laboratories where only a moderate degree of accuracy is required.

by an air-mantle. This ensures a slower and more uniform rate of cooling of the liquid. Through a cork in the neck of C there pass a thermometer, T, and a stirrer, S, to the upper end of which a non-conducting handle of cork or wood is attached. To ensure freedom of movement and guidance to the stirrer, the latter is made to pass through a short piece of glass tubing inserted in the cork of the freezing-point tube.

In order to keep the temperature of the cooling bath more uniform, it is well to surround the latter and to cover the lid with thick felt.

Precautions.—Special mention may be made here of a few precautions which should be observed in all determinations of the molecular weight by this method :—

1. *The temperature of the cooling bath must not be too low.*

When one considers the factors affecting the temperature of the liquid in the freezing-point tube, it is seen that they are (chiefly) three in number, viz. abstraction of heat by the cooling bath ; addition of heat from the outside by conduction through the stirrer, thermometer, etc. ; addition of heat (latent heat of fusion) to the liquid by the solidifying solvent. If, for the moment, it is supposed that no solidification takes place, it will be evident that the final temperature of the liquid will be the resultant of the action of the first two factors. This temperature, called the *convergence temperature*, will, of course, be all the lower, the lower the temperature of the cooling bath ; and it will also, in general, lie below the true freezing-point of the liquid. If, now, in this supercooled liquid, solid begins to form, the latent heat of fusion will be added to the liquid, and the temperature will therefore rise. But the temperature which is now reached will not necessarily be the true freezing-point of the liquid, for it is the resultant of two opposing factors, viz. the rate at which heat is withdrawn (which in turn depends on the difference between the temperature observed and the convergence temperature), and the rate at which heat is given to the liquid, which will depend on the latent heat of fusion and on the velocity of crystallization. Since the velocity of crystallization may be taken as being proportional to the degree of supercooling, it is clear that the final observed temperature will be lower than the true freezing-point by an amount directly proportional to the difference between the observed temperature and the con-

vergence temperature, and by an amount inversely pro-portional to this difference ; that is—

$$T = t + \frac{k}{K}(t - t')$$

where T is the true freezing-point, t the observed freezing-point, t' the convergence temperature, k a constant depending on the rate of abstraction of heat, and K a constant depending on the rate of addition of (latent) heat.[1]   In order to diminish the value of the correction $\frac{k}{K}(t - t')$, the temperature difference $(t - t')$ should be made small.   This is the reason why the temperature of the cooling bath should not be too low.   To obtain the accuracy aimed at here, the temperature of the cooling bath should not exceed 3° or 4° below the freezing-point of the liquid.

2. *The amount of supercooling should not exceed* 0·3°–0·5°.

From the equation given above, it will be seen that the value of the correction $\frac{k}{K}(t - t')$ can also be diminished by increasing the value of K, *i.e.* by increasing the degree of supercooling and so obtaining the separation of a large amount of the solid solvent.   If this is done, however, the concentration of the solution is appreciably altered, and the depression of the freezing-point is therefore apparently too great.[2]   For ordinary purposes, the above limits of super-cooling may be taken.

3. *The stirring should not be too rapid, and should be as uniform as possible.*

The stirring should be just sufficiently rapid to maintain the contents of the tube at a uniform temperature.   Too rapid stirring should be avoided, so as not to give rise to too much heat by friction.   An up-and-down movement of the stirrer at the rate of about once per second will be sufficient.

4. *Always tap the thermometer before taking a reading.*

As the bore of the capillary of the thermometer is very

[1] Nernst and Abegg, *Z. physikal. Chem.*, 1894, **15**, 681.
[2] The change in the concentration can be calculated as follows : If c is the specific heat of the liquid, l the latent heat of fusion, t the amount of supercooling in degrees Centigrade, then the fraction of the total amount of liquid which will solidify will be $\frac{ct}{l}$, so that instead of there being W g. of solvent to w g. of solute, there will now be $W\left(1 - \frac{ct}{l}\right)$.

small, the mercury is inclined to "hang," and the purpose of tapping the thermometer with the finger or a small padded hammer is to overcome this.

The Beckmann Thermometer.—In order that the determination of the molecular weight shall be made with sufficient accuracy, it is necessary to be able to read the temperatures with an error not exceeding 0·001–0·002°. The thermometer should therefore be graduated in, at least, hundredths of a degree. Such a thermometer, however, if made in the ordinary way, would have only a very short range unless its length were made inconveniently great. It would be necessary, therefore, to have a number of these thermometers for use at different temperatures. To obviate this necessity, a thermometer was designed by Beckmann, which, although it does not allow of the absolute temperature being read, enables one to determine differences of temperature at any desired absolute temperature.

The *Beckmann thermometer* (Fig. 61) as usually employed in the laboratory has a range of only five or six degrees ; and is generally graduated in degrees, tenths and hundredths of a degree. The peculiarity of the Beckmann thermometer is that the amount of mercury in the bulb, and therefore the temperature at which the thermometer can be used, can be altered. The lower the temperature, the greater must be the quantity of mercury in the bulb.

This regulation of the amount of mercury in the bulb is rendered possible by having at the upper end of the capillary a small reservoir, R, into which the excess of mercury can be driven, or from which a larger supply of mercury can be introduced into the bulb.

Setting the Beckmann Thermometer.—Before using the Beckmann thermometer, it must be "set," *i.e.* the amount of mercury in the bulb must be regulated so that at the particular temperature of the experiment, the end of the mercury thread is on the scale. This is done as follows :—

Hang the thermometer in a beaker of water the temperature of which is regulated, according to the

FIG. 61.

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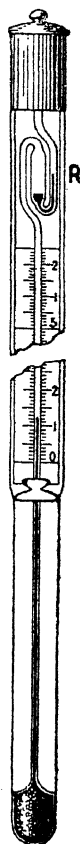
experiment,[1] with the help of an ordinary thermometer graduated, preferably, in fifths or tenths of a degree,[2] and see whether or not the top of the mercury of the Beckmann thermometer stands on the scale. If it does not, then suppose in the first place that it does not rise so far as the scale ; that is, suppose there is too little mercury in the bulb. In this case, place the thermometer in a bath the temperature of which is sufficiently high to cause the mercury to pass up to the top and to form a small drop at the end of the capillary. Now invert the thermometer, and tap it gently so as to collect the mercury in the reservoir at the end of the capillary and to join with the mercury there. Return the thermometer carefully, without shaking, to the upright position, and place the bulb again in the first bath, regulated at the proper temperature. The mercury in the bulb will contract and draw in more mercury from the reservoir. After several minutes, when the thermometer will have taken the temperature of the bath, strike the upper end of the thermometer against the palm of the hand so as to cause the excess of mercury to break off from the end of the capillary. Make sure, now, that the amount of mercury has been properly regulated, by placing the thermometer in a bath the temperature of which is equal to the highest that will occur in the experiment, and see that the mercury stands on the scale. If it stands above the scale, too much mercury has been introduced, and some of it must be got rid of by driving the mercury once more up into the reservoir and shaking off a little of it from the end of the capillary. Of course, if the mercury is found to stand too low on the scale, then more mercury must be introduced into the bulb in the manner described above, these operations being repeated until the proper amount of mercury has been introduced. *This must always be tested by placing the thermometer in a bath at the temperature of the experiment and making sure that the mercury remains on the scale.*

On account of the so-called " thermal after-effects " met with in the case of glass, owing to which glass, after being heated, does not immediately acquire its original volume

[1] Since the scale of the Beckmann thermometer does not extend upwards to the end of the capillary, the temperature of this bath must be at least 2°–3° *higher* than the highest temperature to be met with in the experiment.

[2] The accuracy of this thermometer should be tested previously by comparison with a standard thermometer.

it is advisable to have at least two Beckmann thermometers, one for use at lower, the other for use at higher tempera-tures.

EXPERIMENT.—*Determination of the Molecular Weight of a Substance in Benzene.*

First set up the apparatus (p. 126) completely, to make sure that the different parts fit properly ; and see that the stirrer in the freezing-point tube works smoothly without striking against the bulb of the thermometer.   Remove the thermometer and stirrer from the freezing-point tube, and fit the latter, which must be clean and dry, with an unbored cork.   Weigh this tube, and then pour in 15–20 g. of pure benzene, and weigh again.   For this purpose a balance weighing to a centigram should be used.[1]   Now set the Beckmann thermometer so that at the temperature of 5·4° (melting-point of benzene) the mercury stands not lower than the middle of the scale.   Dry the thermometer thoroughly and insert it, along with the stirrer, in the freezing-point tube, so that the bulb of the thermometer is completely immersed in the benzene.   Fill the vessel A with water and ice, so that a temperature of about 2°–3° is obtained.   This can be regulated by varying the amount of water and ice. The freezing-point of the benzene is then determined.

In doing this, make a first approximate determination by placing the freezing-point tube directly in the cooling bath,[2] so that the temperature falls comparatively rapidly. When solid begins to separate, quickly dry the tube and place it in the air-mantle in the cooling bath ; stir slowly and read the temperature when it becomes constant.   Now withdraw the tube from the mantle and melt the solid benzene by means of the hand.   If in this operation the temperature of the liquid is raised more than about 1° above the freezing-point, place the tube again directly in the cooling bath and allow the temperature to fall to within about half a degree of the freezing-point as determined above ; quickly dry the tube and place it in the air-mantle and allow the temperature to fall, stirring slowly all the while.   When the temperature has fallen to from 0·2° to 0·5° below the approxi-

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[1] More simply, but less accurately, pipette into the freezing-point tube a known volume, say 25 ml., of benzene.   The mass of this can be obtained by multiplying the volume by the density.   In this way the weighing of a rather awkward piece of apparatus is avoided.

[2] For this purpose push the lid of the bath aside ; do not remove it from the bath.

mate freezing-point found above, stir more vigorously. This will generally cause the crystallization of the benzene to commence, and the temperature will begin to rise.[1] Stir slowly again, and, with the help of a lens, read the temperature every few seconds, tapping the thermometer firmly with the finger each time before doing so. Note the highest temperature reached. Again melt the solid benzene which has separated out, and redetermine the freezing-point in the manner just described. Not fewer than three concordant readings of the freezing-point should be made, the mean of these being then taken as the freezing-point of the benzene. The deviations of the separate readings from the mean value should not exceed 0·002°.

The freezing-point of the solvent having been determined, a weighed amount of the substance (*e.g.* camphor, naphthalene), compressed into tablet form, is now introduced into the benzene through the side tube D of the apparatus.[2] The amount taken should be sufficient to give a depression of the freezing-point of not less than 0·2°. After the substance has dissolved, the freezing-point of the solution is determined in exactly the same manner as described for the pure solvent ; first an approximate and then not fewer than five accurate determinations being made. In each case note the degree of supercooling.

Two further additions of the substance should be made, and the freezing-point of the solution determined after each addition. The total depression of the freezing-point should not exceed about 0·5°. From each set of determinations, calculate the molecular weight of the solute.[3] The error should not exceed 3–5 per cent.

[1] It is sometimes found that crystallization does not commence in the supercooled liquid, even on stirring vigorously. In such cases too great supercooling should be avoided by the introduction of a small crystal of the solid solvent through the side tube D, the stirrer being raised and touched by the crystal. In cases, therefore, where supercooling readily occurs, it is well to have a tube containing a small quantity of the solidified solvent standing in the cooling bath.

[2] Where a tablet press is not available, the substance may be shaken out from a weighed tube inserted through D.

[3] If solutions are employed which give a depression of more than 0·5°, the molecular weight should be calculated by the more accurate expression $d = k \cdot \dfrac{n_2}{n_1 + n_2} = k \cdot \dfrac{wM}{wM + Wm}$, or $m = \dfrac{wM(k - d)}{d \cdot W}$. In these expressions, $\dfrac{n_2}{n_1 + n_2}$ is the molar fraction of the solute, M is the molecular weight of the solvent, and k has the value $\dfrac{K}{M}$, where K is the ordinary freezing-point constant (See Brown and Bury, *J. Chem. Soc.*, 1924, **125**, 2219.)

Further Calculations.—From the determinations of the freezing-points of the benzene solutions, calculate (*a*) the freezing-point constant, and (*b*) the latent heat of fusion of benzene, the theoretical molecular weight of the solute being assumed.

Activity of the Solute.—Determinations of the freezing-points of solutions enable one to calculate what is called the *activity* or true " active mass " or " effective concentration " of a substance in solution, the " concentration " which should be used in applications of the law of mass action to reactions in solution, and in thermodynamical calculations. For solutions of concentration lower than about 3-molal (*i.e.* 3 gram-molecules of solute per 1000 *grams* of solvent), the activity of the solute can be calculated by means of the expression,[1] $2 \cdot 303 \log_{10} \dfrac{a}{m} = -2\left(1 - \dfrac{\theta}{\lambda m}\right)$, where *a* is the activity of the solute, *m* is the molal concentration (gram-molecules per 1000 grams of solvent), θ is the depression of the freezing-point and λ is the molecular lowering of the freezing-point (per 1000 grams of solvent), at infinite dilution. λ for water is 1·858.

EXPERIMENT.—*Determine the Freezing-points of Aqueous Solutions of Mannitol or of Carbamide over a Range of Concentrations.*

In the case of aqueous solutions, a mixture of salt solution and ice should be used in the cooling bath, and the temperature regulated to about $-3°$ by adjusting the concentration of the salt solution. To lower the temperature, increase the concentration of the solution. Ice must always be present.

From the results obtained, calculate (*a*) the molecular weight of the solute, (*b*) the molecular depression of the freezing-point per 1000 grams of solvent, (*c*) the activity of the solute.

Abnormal Molecular Weights.—In the case of a number of substances (very commonly in the case of organic acids and hydroxy-compounds in benzene), it is found that the molecular weight determined by the cryoscopic method is greater than that calculated from the usual chemical formula of the substance, by an amount exceeding the experimental error. One is therefore led to assume that these substances *associate* in solution, *i.e.* two or more molecules combine to

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[1] Lewis and Randall, *Thermodynamics*, chap. xxiii.

form a larger molecule. As an example of this, one may take the case of benzoic acid (C_6H_5.COOH) in benzene.

EXPERIMENT.—*In the manner previously described, determine the apparent Molecular Weight of Benzoic Acid in Benzene, and from the numbers obtained calculate the Degree of Association, assuming that two single molecules combine to form one compound molecule.*

The degree of association can be calculated in the following manner : If x represents the degree of association, or the fraction of the total number of molecules which combine to form larger molecules, and if n represents the complexity of the new molecules, then of each gram-molecule of substance taken there will be $1-x$ gram-molecules unassociated, and x/n gram-molecules associated. Consequently, instead of there being 1 gram-molecule there will be only $1-x+x/n$ or $1-x\left(1-\dfrac{1}{n}\right)$. In other words, the number of dissolved molecules has decreased in the ratio of $1 : 1-x\left(1-\dfrac{1}{n}\right)$. But the depression of the freezing-point is proportional to the number of gram-molecules (in a given weight of solvent) ; hence, if d_t represent the depression calculated on the assumption of no association, and d_0 the depression actually obtained—

$$\frac{d_0}{d_t} = \frac{1-x\left(1-\dfrac{1}{n}\right)}{1}, \text{ or } x = \frac{}{d_t\left(1-\dfrac{1}{n}\right)}$$

Not only can the molecular weight determined from the depression of the freezing-point have a value greater than that corresponding with the ordinary chemical formula of the substance, but it can also have a value much smaller, thus pointing to a *dissociation* of the molecules in solution. This is found, for example, in the case of salts, acids, and bases in aqueous solution, and, according to the classical theory of Arrhenius, there occurs, in these cases, an electrolytic dissociation of neutral molecules into electrically charged ions. Adopting this theory, one can readily calculate the degree of dissociation or ionization from cryoscopic determinations. Thus, if α represents the degree of dissociation, and if n is the number of dissociated molecules (ions) formed from each molecule of the solute, then the relative increase in the number of molecules (or molecules+ions) in the solution will be as $1 : 1+(n-1)\alpha$, the expression, $1+(n-1)\alpha$, being equal to the van't Hoff coefficient i. Hence, if d_0 represent the observed, and d_t the theoretical

depression (calculated on the assumption of no dissociation), one has—

$$\frac{d_0}{d_t} = \frac{1 + (n-1)\alpha}{1}, \text{ or, } \alpha = \frac{d_0 - d_t}{d_t(n-1)}$$

While the Arrhenius theory may still be accepted as valid for weak acids and weak bases, strong bases and most salts are now regarded as being completely ionized in dilute solution; and the variation of osmotic activity with concentration is regarded as being due, not to a variation in the number of the ions but to variation in their activity resulting from the mutual attraction of oppositely charged ions.

According to this view, it must be noted that in the case of a strong binary electrolyte, the value of α, calculated from the expression $i = 1 + \alpha$, has no very definite significance. It is better, therefore, to calculate the thermodynamic degree of dissociation, or activity coefficient, γ, and this may be done from freezing-point determinations.[1] In the case of strong uni-univalent electrolytes, in concentrations not exceeding 0·01 molal, $\gamma = 1 - 3\left(1 - \frac{\theta}{2\lambda m}\right)$, but in more highly concentrated solutions, more complex expressions must be used.

Cryoscopic Determinations by Analysis of the Equilibrium Solution.—Instead of determining the freezing-point of a solution of known concentration, one may also determine the concentration of the solution which is in equilibrium with ice at a noted temperature. This method is peculiarly suitable for aqueous solutions.[2] The determinatoins are best carried out in a Dewar vacuum vessel of 200–250 ml. capacity, closed by a rubber stopper through which pass a Beckmann thermometer and a stirrer. A glass tube, wide enough to allow the passage of a pipette, also passes through the rubber stopper. While the experiment is in progress, this tube is plugged with cotton wool. The Dewar vessel is packed in a wooden box with animal or cotton wool. The box should also be closed by a lid pierced with holes for the thermometer and stirrer, and for the passage of a pipette. Distilled water, sufficient in amount to cover the bulb of the thermometer, is placed in the Dewar vessel which

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[1] See Lewis and Randall, *Thermodynamics*, chap. xxvii.
[2] See Adams (*J. Amer. Chem. Soc.*, 1915, **37**, 481); Randall and Vanselow (*ibid.*, 1924, **46**, 2422); Hovorka and Rodebush (*ibid.*, 1925, **47**, 1614); Scatchard, Jones and Prentiss, *ibid.*, 1932, **54**, 2676.

is then filled nearly full with broken ice prepared from distilled water. The contents of the vessel are stirred and the equilibrium temperature read as carefully as possible on the Beckmann thermometer. The water is then poured away and about 100 ml. of 0·2–0·3 molal hydrochloric acid, previously cooled to 0° by standing in a jar of ice, are poured into the Dewar vessel. More pure crushed ice is added if necessary. When the temperature has become constant, 20–25 ml. of the solution are withdrawn by means of a fine-pointed pipette, and run into a small weighed flask. The weight of the solution is determined and its concentration then ascertained by titration with baryta solution.

Similar determinations are made with solutions of varying concentration down to 0·01 molal. Determinations may also be carried out with solutions of potassium or sodium chloride, the concentrations of the solutions being determined by titration with silver nitrate.

At each concentration, calculate the apparent degree of dissociation (a) of the electrolyte and also the activity coefficient, γ, by the equation on p. 135.

When the concentration of the solutions cannot be determined by titration, one may employ the refractometric method (p. 118).

Since the depression of the freezing-point gives a measure of the molal concentration of the solute, cryoscopic determinations may be used for throwing light on reactions which may take place between the solute and solvent [1] (hydration or solvation), or changes which may take place in the molecular state of the solute (e.g. association or dissociation), or reactions which take place between solutes (e.g. formation of complex salts). To illustrate this point, one may determine the freezing-point of a solution of potassium bromide (0·5 gram-molecule per litre) to which varying amounts of mercuric bromide (0·1, 0·2, 0·3 gram-molecule per litre) are added.

II. BOILING-POINT (EBULLIOSCOPIC) METHOD

The molecular weight of a substance in solution can also be determined from the elevation of the boiling-point which is produced, provided that the solute is not appreciably volatile at the temperature of the boiling solvent.

If w g. of a substance when dissolved in W g. of a solvent

[1] See Jakowkin, Z. physikal. Chem., 1899, **29**, 613.

raise the boiling-point of the latter by $e°$, the molecular weight of the dissolved substance is given by the expression—

$$M = K \cdot \frac{w}{e \cdot W}$$

in which K is a constant, the value of which depends on the solvent. Its value for a few of the more common solvents is given in the following table :—

Solvent.	Boiling-point (760 mm.).	K	Correction to K per 10 mm.	Heat of vaporization (cal.).
Acetone. . .	56·2°	1720	—	124·5
Benzene . .	80·2°	2570	24	94·4
Chloroform .	61·2°	3860	10	59·0
Ethyl alcohol .	78·5°	1150	10	204·4
Ethyl ether .	34·6°	2110	7	83·9
Water . . .	100°	513	7	539·5

The correction values in the fourth column have to be added to K when the barometric pressure is above 760, and subtracted when the pressure is below 760 mm.

Apparatus with Electrical Heating.—The older forms of the Beckmann apparatus, designed for heating by gas, have now been superseded by other forms of apparatus which are more convenient to handle, and which give more rapid and accurate results. Of these, the apparatus designed for electrical heating, and first suggested by S. L. Bigelow,[1] possesses, in ordinary laboratory practice, a number of advantages ; and its use is to be recommended, more especially when dealing with non-electrolytic solutions. In this apparatus (Fig. 62) the boiling-point tube, A, is fitted with a cork through which pass a Beckmann thermometer, T, and two copper wires, WW, to the ends of which a spiral of platinum or nichrome wire (No. 26) is attached. Binding screws, for connecting to leads from a battery, are fitted to the free ends of the copper wires, which also, for the sake of rigidity and to prevent damage to the spiral, are bound to an insulated rod, R. The platinum spiral should be placed near to the bottom of the boiling-point tube, which, when in use, is supported by means of a cork in a silvered Dewar vacuum vessel, V. A condenser, C, inserted in the

[1] *Amer. Chem. J.*, 1899, **22**, 280.

side-tube, B, serves to condense the vapour of the boiling solvent.

In carrying out a determination of the elevation of the boiling-point, a weighed amount of solvent is placed in the boiling tube (cf. p. 131), and the cork with heating spiral and thermometer, previously adjusted for the solvent, is
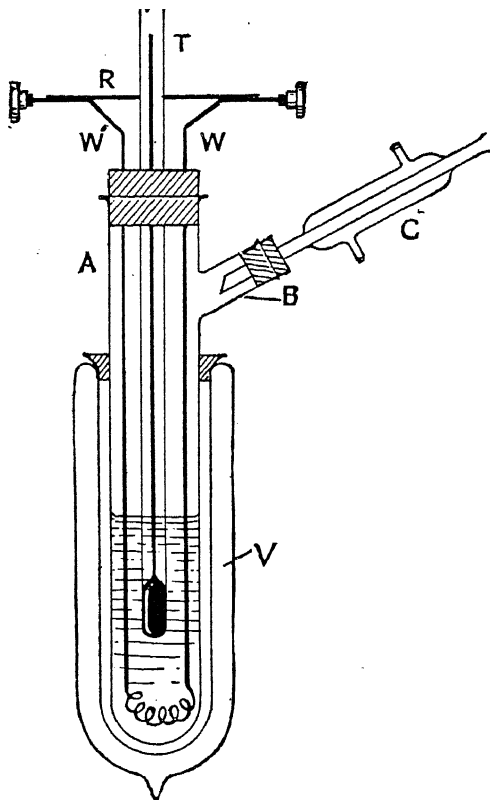
FIG. 62.

inserted in the tube. The bulb of the thermometer must be completely immersed in the liquid. The solvent is then raised to its boiling-point by the passage of an electric current through the heating spiral, and when the boiling-point is reached, the strength of current should be adjusted by means of a resistance, so that the liquid is kept boiling regularly and vigorously. When the temperature has

become constant, the thermometer, after being firmly tapped with the finger, is read as accurately as possible with the help of a lens. This gives the boiling-point of the solvent.

The heating current is now stopped, and after the condensed vapour has ceased to drop from the condenser, the latter is removed, and a weighed amount of solute introduced through the tube B. The condenser is again fitted to the apparatus, the heating current is passed through the spiral and the boiling-point of the solution determined.

Two further quantities of the substance should be introduced, and the boiling-point determined after each addition. From the boiling-points of the pure solvent and of each of the solutions, the molecular weight is calculated for each concentration. In making the calculation, 0·2 g. should be subtracted from the weight of solvent taken, when this is benzene, ether, acetone, etc., to allow for the vapour contained in the tube and condenser.

On account of the influence of pressure on the boiling-point, the barometric pressure at the beginning and end of the experiment should be noted, and, if necessary, a correction applied.[1] At times of rapidly changing barometric pressure, it is better to avoid the necessity for making this correction by having a second apparatus in which the pure solvent is kept boiling.

In the case of the determination of the molecular weight of liquids, the latter are introduced into the boiling-tube by means of a pipette with long tube (Fig. 63).

EXPERIMENT.—*Determine the Molecular Weight of Camphor or of Anthracene in Benzene, or of Azobenzene in Chloroform.*

EXPERIMENT.—*Determine the Molecular Weight of Ethyl Benzoate in Benzene.*

Calculation.—Assuming the theoretical molecular weight of the solute, calculate, from the measurements made, the heat of vaporization of the solvent and the value of the boiling-point constant (p. 137).

Cottrell's Apparatus.—An improved boiling-point apparatus has been designed by Cottrell [2] for the purpose of

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[1] If an increase, dB, of the barometric pressure occurs, one subtracts from the elevation of the boiling-point found, the quantity $\left(\dfrac{d\mathrm{B}}{\mathrm{B}} \cdot \dfrac{K}{M}\right)$, where B is the mean barometric pressure, K the boiling-point constant, and M the molecular weight of the solvent in the vapour state.

[2] *J. Amer. Chem. Soc.*, 1919, **41**, 721. This apparatus was modified and used by Washburn and Read (*ibid.*, p. 729) for the accurate determination of the boiling-points of solutions. See also Spencer (*ibid.*, 1921, **43**,

securing a more perfect equilibrium between the solution and the vapour and of enabling the temperature of the equilibrium to be accurately determined when both phases are under the same external pressure. With this apparatus fluctuations of temperature and errors of temperature determination due to superheating, etc., are avoided.

The apparatus (Fig. 64) consists of a boiling-tube A, into the neck of which fits the hollow stopper B. The walls of the stopper are prolonged downwards so as to form a cylinder enclosing the bulb of the Beckmann thermometer [1]
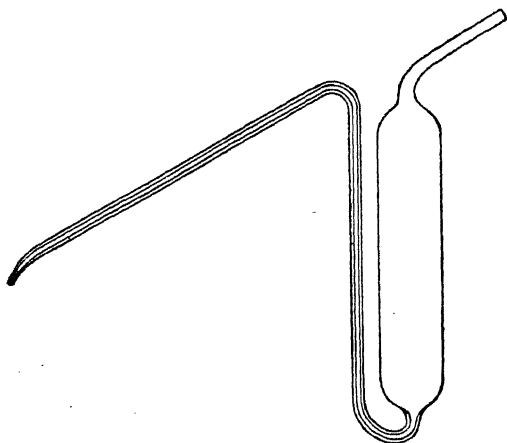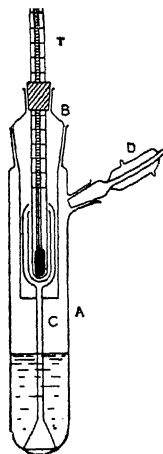
FIG. 63.   FIG. 64.

T, and the branches of the " pump " tube C. The cylinder serves as a jacket for the thermometer and prevents the liquid, flowing from the condenser D, coming into contact with the thermometer. The pump tube C divides as shown into two, or preferably three, branches, arranged symmetrically, and surrounding the lower end of the thermometer ; and the upper, open ends of the tubes are bent so that the openings face the stem of the thermometer. The funnel of the tube rests on the bottom of the boiling-

301). Modifications of the Cottrell apparatus have also been introduced by Swietoslawski (*Bull. Soc. chim. France*, 1927, **41**, 717), by Rupe and Wassiliev (*Helv. chim. acta*, 1928, **11**, 713), and by Bancroft and Davis (*J. Physical Chem.*, 1929, **33**, 591). See also Davis, *J. Chem. Ed.*, 1933, **10**, 47 ; Gordon, *ibid.*, p. 489.

[1] A differential thermometer for use with this apparatus has been described by Menzies and Wright, junr., *J. Amer. Chem. Soc.*, 1921, **43**, 2314.

tube, and it is advisable that the rim of the funnel should be notched or have little glass beads fused on it, so as to prevent too complete contact and a consequent locking of the liquid.

In using this apparatus the solvent (in known amount) is caused to boil by means of a flame protected from draughts. When the liquid boils, the bubbles of vapour which form under the funnel rise up in the narrow tube, carrying with them liquid which is then projected against the stem of the thermometer. The bulb of the thermometer is, in this way, kept bathed in the boiling liquid which is pumped up by the vapour bubbles and which is in equilibrium with the vapour in the apparatus. By this means a constant temperature (boiling-point) is soon attained, and the temperature remains very steady. After determining the boiling-point of the pure solvent, a weighed pellet of the solute is introduced by way of the condenser, and the boiling-point of the solution determined in the same way as for the solvent.

Sakurai-Landsberger Method.—For general chemical purposes where an accuracy of 5–10 per cent. is sufficient, a modification of the Sakurai-Landsberger method may be employed. In this case the solution is heated by means of the vapour of the boiling solvent, and the method has the advantage that several determinations of the molecular weight can be carried out with one and the same sample of material, so that only one weighing is necessary. Further, instead of determining the amount of solvent by weight, its amount by volume is measured. This makes no difference in the expression for the calculation of the molecular weight, except that a different constant is employed, which is equal to the ordinary boiling-point constant divided by the density of the solvent at its boiling-point. Thus $M = K' \dfrac{w}{e \cdot v}$, where K' is a constant for the solvent employed, w is the weight of the solute in grams, e is the elevation of the boiling-point, and v is the volume of the solution. The values of some of the constants are as follows :—

Solvent.	Boiling-point.	K'.	Solvent.	Boiling-point.	K'.
Acetone .	56·5°	2220	Chloroform	61·2°	2600
Alcohol .	78·3°	1560	Ether .	34·6°	3030
Benzene .	80·2°	3280	Water .	100·0°	540

Apparatus of McCoy.—Of the various forms of apparatus which have been devised, one of the most convenient, for ordinary laboratory work, is that due to McCoy.[1] This apparatus (Fig. 65) consists of a tube, B, which serves both as a boiling-tube and as a vapour jacket. Inside this there passes the narrower tube A, which is graduated from the volume 10 ml. to the volume 35 ml., from the closed end of the tube. Sealed into the wall of A is the narrow tube *ab*, the lower (closed) end of which is perforated with a number of small holes. The graduated tube A is fitted with a cork carrying a Beckmann thermometer, and a side tube, *c*, connects it with a condenser, C.
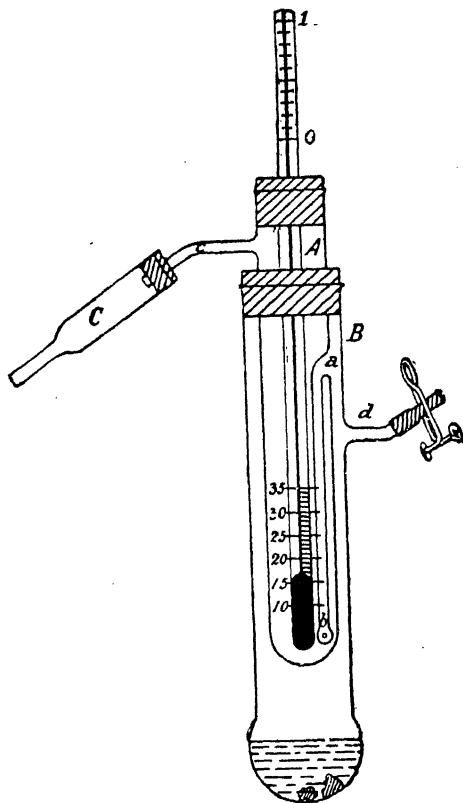
FIG. 65.

EXPERIMENT.— *Determine the Molecular Weight of Benzoic Acid in Acetone and in Ethyl Alcohol.*

About 50 ml. of pure solvent are placed in B, together with a piece of porous tile, to ensure steady ebullition; 12–15 ml. of the solvent are also placed in the graduated tube A, and the apparatus then fitted together as shown in the figure. The solvent in B is caused to boil, while the side tube *d* is closed by a clip.[2]

[1] *Amer. Chem. J.*, 1900, **23**, 353. Other modifications of the apparatus have been described by Beckmann (*Z. physikal. Chem.*, 1905, **53**, 17), Turner (*J. Chem. Soc.*, 1910, **97**, 1184), and Ludlam (*ibid.*, 1902, **81**, 1194).
[2] In the case of inflammable liquids, more especially, electrical heating should, when possible, be used. For this purpose a current of electricity

As the vapour rises in the tube B it heats the solvent in the inner graduated tube, and then forces its way through the narrow tube *ab* into the liquid in the inner tube, and raises its temperature to the boiling-point. The rate of boiling in the outer tube should now be adjusted so that the solvent in the inner tube boils slowly but regularly, and a very slow distillation into the condenser takes place.

When the thermometer registers a constant temperature, the reading is taken as the boiling-point of the pure solvent.

The clip on the side tube *d* is now opened, and the heating of the liquid in the outer tube interrupted. (The side tube *d* is opened *before* the heating is interrupted, otherwise liquid may be sucked over from the inner tube through *ab* owing to the cooling down of B.)

A weighed amount of substance, the molecular weight of which is to be determined, is now introduced into the inner tube, and the above method of procedure repeated until a constant boiling-point is again obtained. After reading off the boiling temperature of the solution, tube *d* is again opened and the boiling in B stopped. The thermometer is carefully raised out of the solution, and the volume of the latter is read.

After replacing the thermometer a fresh determination of the boiling-point can be made exactly as explained above. Owing to the condensation in the inner tube of a certain quantity of the solvent vapour, the concentration of the solution, and consequently the boiling-point, will show a change in each successive determination, so that one thereby obtains a series of boiling-points corresponding to different concentrations, from which the molecular weight of the solute can be calculated. Owing, however, to the fact that the liquid in the inner tube is raised to near its boiling-point by the vapour in the tube B, the amount of condensation, and consequently the change in concentration produced is comparatively small, and will depend on the ratio of the latent heat of vaporization to the specific heat of the solution. In some cases (*e.g.* water) it may be necessary to add small quantities of the solvent to the solution in

may be passed through a spiral of resistance wire, placed in the liquid in the tube B ; or, the boiling tube may be placed on an electrical hot plate. For the latter method of heating the cheap asbestos-woven wire resistance nets now obtainable serve admirably.

the inner tube in order to obtain a series of different concentrations.

The molecular weight of benzoic acid is calculated by the formula on p. 141.

One may also determine the molecular weight of naphthalene in benzene and of carbamide in water.

CHAPTER IX

DISTRIBUTION OF A SUBSTANCE BETWEEN TWO NON-MISCIBLE SOLVENTS

An operation which is frequently practised, especially in organic chemistry, is that of extracting a substance from its aqueous solution by means of ether. The underlying principle of this method is that when a substance is shaken with two non-miscible solvents, it is distributed between them in a definite manner, which depends on the solubility of the substance in each of the solvents separately.

The ratio in which the solute is distributed between the two solvents depends, however, not only on its solubility in each, but also on whether or not it possesses the same molecular weight in the two solvents; and for this reason, the study of the relationships which obtain here is of importance in chemistry, as affording a means of determining the state of association or dissociation of a substance in solution.

I. *The solute has the same molecular weight in each of the solvents.*

When the solute has the same molecular weight in each of the solvents, it is distributed between them in a ratio which depends on the temperature, but is independent of the absolute concentration.[1] Hence, if c_1 denote the concentration (in gram-molecules per litre) of the solute in the first solvent, and c_2 the concentration in the second solvent, then when equilibrium has been established between the two solutions, the ratio c_1/c_2 has a constant value, provided the temperature is constant. The value of this ratio is called the *coefficient of distribution* or the *coefficient of partition*.

EXPERIMENT.—*Determine the Coefficient of Distribution of Succinic Acid between Ether and Water.*

[1] The distribution law, however, is strictly valid only in the case of very dilute solutions.

No special apparatus is required for this experiment; a bottle, preferably tall and narrow, furnished with a well-fitting glass or rubber stopper, may be used. In the bottle place 100–150 ml. of an aqueous solution [1] (approximately 1 per cent.) of succinic acid, and add an equal volume of ether, and then immerse the bottle up to the neck in a thermostat, the temperature of which is maintained constant, say at 25°. The bottle should be kept in the thermostat for about half an hour, and should be shaken vigorously every four or five minutes. After a final shaking, a rotatory motion is imparted to the solutions, in order to loosen any drops of liquid which may adhere to the sides of the bottle, and the bottle again placed upright in the thermostat until complete separation into two layers has taken place. The concentration of the acid in the ethereal layer is then determined by removing the solution by means of a pipette, and titrating with 0·05N or 0·025N baryta solution (p. 153), using phenolphthalein as indicator. The end of a bent capillary tube is then placed in the aqueous solution, and the latter siphoned off into a clean flask, and also titrated with baryta solution. The first millilitre or so of the aqueous solution should be rejected.

Having determined the concentrations of succinic acid in the aqueous and ethereal solutions, repeat the determination as above for different total concentrations, using approximately 0·5 and 0·25 per cent. aqueous solutions to start with.

Tabulate the values of c_1, c_2, and c_1/c_2 obtained in each case.

II. *The molecular weight of the solute in the two solvents is different.*

If, in the one solvent, the solute has the normal molecular weight, but in the second solvent is partially associated according to the equation—

$$n(A) \rightleftharpoons (A)_n,$$
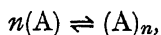
then, at a given temperature, the ratio c_1/c_2 will no longer be constant.

According to the law of partition, however, there exists a constant ratio of partition for each class of molecule;

[1] In this, as in all the other experiments in this chapter, distilled water free from carbonic acid should be employed. For method of preparation, see p. 153.

hence a constant ratio should be found between the concentration of the *single* molecules in the first solvent and the *single* molecules in the second solvent. But, according to the law of mass action, the concentration of the single molecules in the second solvent is proportional to the nth root of the total concentration (provided that the degree of association is large) ; and therefore, if c_1 is the concentration of the solute in the first solvent, and c_2 the concentration in the second, the ratio $c_1/\sqrt[n]{c_2}$ should be a constant.

EXPERIMENT.—*Determine the Partition Coefficient of Benzoic Acid between Water and Benzene, or between Water and Chloroform, at 25°.*

The determination is carried out as described for the preceding experiment. Three solutions of benzoic acid in benzene, of strengths approximately 10, 6, and 4 per cent., should be prepared ; for each determination 50 ml. of the benzene solution and an equal volume of water (free from carbonic acid) should be shaken together, and 10 ml. removed for titration.

Since, at the concentrations given above, the benzoic acid exists for the most part as associated molecules $(C_6H_5.COOH)_2$ in the benzene solution, the ratio $c_1/\sqrt{c_2}$ should be found constant.

Tabulate the values of c_1, c_2, c_1/c_2, and $c_1/\sqrt{c_2}$.

Determination of the Molecular Weight of Dissolved Substances.

From what has been said, it will be evident that from a study of the ratio of distribution of a substance between two non-miscible solvents, the *relative* molecular weight of the substance in the two solvents can be determined. Further, from the change, if any, in the value of the partition coefficient with concentration, valuable information, quantitative as well as qualitative, can be obtained with regard to the change in molecular weight, owing to association or dissociation, in the two solvents. To illustrate this, the following experiments should be performed :—

EXPERIMENT.—*Determine the Change in the Value of $c_1/\sqrt{c_2}$ with Concentration in the Distribution of Benzoic Acid between Water and Benzene, and calculate therefrom the Dissociation Constant of $(C_6H_5.COOH)_2$.*

It has just been found that in fairly concentrated solutions

of benzoic acid, the ratio $c_1/\sqrt{c_2}$ in water and benzene is constant at constant temperature. On passing to more and more dilute solutions, however, two factors affect the constancy of this ratio to an increasing extent. These are, the increasing ionization of the benzoic acid in the aqueous solution, and the dissociation of the double into single molecules in the benzene solution. The value of the latter factor can be determined from the change in the value of the partition coefficient in dilute solutions.

Let c_1 = the concentration in the aqueous phase,
c_2 =   ,,   ,,   benzene phase,
a = the degree of ionization of the acid in water,

and, therefore, $c_1(1-a)$ = the concentration of the normal un-ionized molecules in the aqueous phase.

If k is the affinity constant of the acid (see Chap. X), one has—

$$k = \frac{a^2}{(1-a)v}$$

where v is the volume in litres containing 1 gram-molecule of acid. Hence—

$$1 = \frac{kv}{2}\left(\sqrt{1+\frac{4}{kv}} - 1\right)$$

(For benzoic acid $k = 6 \times 10^{-5}$.)

Further, according to the law of partition, the ratio of concentrations of the single molecules in the two solutions is constant. Therefore, if m = concentration of the *single* molecules in benzene—

$$\frac{c_1(1-a)}{m} = K; \text{ or, } m = \frac{c_1(1-a)}{K}$$

On applying the law of mass action to the dissociation of the double into single molecules, one finds (since c_2-m is the concentration of the double molecules)—

$$m^2$$

Hence, from the equation $m = \frac{c_1(1-a)}{K}$, we obtain—

$$K' = \frac{\{c_1(1-a)\}^2}{K^2 \cdot c_2 - c_1(1-a)K}$$

Since K' is constant independently of the concentration,

it follows that, for any other concentrations c'_1 and c'_2 in the aqueous and benzene solutions—

$$\frac{\{c'_1(1-a')\}^2}{K^2c'_2-c'_1(1-a')K}=K'=\frac{\{c_1(1-a)\}^2}{K^2c_2-c_1(1-a)K}$$

With the help of these two equations, the value of K can be calculated. From the value of K one can obtain the value of m, and hence also the value of K', the dissociation constant of the complex molecules.

The measurements are to be carried out in the manner explained above, the concentrations of the benzoic acid in the aqueous and benzene solutions being determined by titration with baryta ($0 \cdot 02N$ to $0 \cdot 01N$), using phenolphthalein as indicator. Water free from carbonic acid must be used in all cases.

The first determination should be made by shaking 200 ml. of a benzene solution containing about 5 g. of benzoic acid with 200 ml. of water, and withdrawing 50 ml. for a titration. After each titration replace the solutions removed by equal volumes of water and benzene.

A series of three or four determinations should be made, and the value of K' calculated for the different concentrations. The deviations from the mean should not exceed 3-5 per cent.

Instead of studying the distribution of benzoic acid between water and benzene, one may, as alternatives, study the distribution of benzoic acid between water and chloroform, of salicylic acid between water and benzene, or of salicylic acid between water and chloroform.

DETERMINATION OF THE DEGREE OF HYDROLYSIS OF SALTS

Since in the aqueous solution of a salt of a weak base and a strong acid, or of a weak acid and a strong base, there is an equilibrium between the salt, the free base and the free acid, this equilibrium can be determined by studying the partition of the weak base or weak acid between water and another solvent, such as benzene or chloroform.

Thus, if an aqueous solution, say of aniline hydrochloride, which is partially hydrolyzed into aniline and hydrochloric acid, is shaken with benzene, the free aniline will distribute itself between the water and the benzene in the ratio of the partition coefficient. Hence, from the concentration of the aniline in the benzene solution, the concentration of the free

aniline, and from this the degree of hydrolysis in the aqueous solution, can be calculated in the following manner :—

The hydrolysis of a salt is represented by the equation—

$$salt + water \rightleftharpoons base + acid$$

and for all mixtures of acids and base, or of salt and water, the equilibrium is given by Guldberg and Waage's law of mass action as—

$$m_1 . m_2 = k . m_3 . m_4$$

where m_1, m_2, m_3, m_4 are the concentrations of base, acid, salt, and water respectively. Since the concentration of the water remains practically constant, m_4 is constant, and therefore $k . m_4$ is also constant, and equal, say, to K.

Let c_1 = initial amount of hydrochloric acid.

c_2 =   ,,   ,,   aniline (or weak base).

c = concentration in g.-equivalents per litre of the weak base in the aqueous layer.

F = coefficient of distribution of the base between water and the other solvent, say benzene.

q = volume of benzene employed per 1000 ml. of water.

Then, when equilibrium is established, $c = m_1$. But if there are c g. in 1000 ml. of the aqueous solution, there must be cqF g. in the benzene solution. Hence, the total quantity of free base is $c(1 + qF)$. The initial amount of base was c_2, hence there must be $c_2 - c(1 + qF)$ g. of the base in the form of the salt (existing in the aqueous layer only). The concentration of the salt is therefore $m_3 = c_2 - c(1 + qF)$. There must, of course, be an equivalent amount of acid in combination, and as the initial amount was c_1, the amount of combined acid must be $c_1 - c_2 + c(1 + qF)$ g. As the salt exists only in the aqueous layer (1000 ml. in volume), the concentration of the acid is $m_2 = c_1 - c_2 + c(1 + qF)$. Substituting these values for m_1, m_2, and m_3 in the above equation, one obtains—

$$c\{c_1 - c_2 + c(1 + qF)\} = K . \{c_2 - c(1 + qF)\}$$

$$\text{or} \quad K = \frac{c\{c_1 - c_2 + c(1 + qF)\}}{c_2 - c(1 + qF)}$$

If the acid and base are taken in equivalent proportions, *i.e.* if one dissolves the salt in water, then $m_1 = m_2$, and $m_3 = c_2 - m_1$. Hence—

$$m_1^2 = K . (c_2 - m_1)$$

Having obtained the value of K, and knowing the value of c_2, m_1 can be calculated. But the degree of hydrolysis is the ratio of free base actually present to what would be present if no salt formation took place, $i.e.$ if the whole of the base taken remained free. The degree of hydrolysis is therefore given by m_1/c_2, or the percentage hydrolysis by $100\,m_1/c_2$.

EXPERIMENT.—*Determine the Percentage Hydrolysis of Aniline Hydrochloride at 25°.*

The partition coefficient, F, of the free base between water and benzene must first be determined. For this purpose, shake up a known quantity of aniline with a mixture of 1000 ml. of water and 60 ml. of benzene in a bottle, placed in a thermostat at 25°. After equilibrium has been established, allow the layers to separate and withdraw 50 ml. of the benzene layer. Into this solution pass dry hydrogen chloride, in order to precipitate the aniline as hydrochloride, and evaporate off the benzene by gently heating on the water bath, at the same time drawing a current of air over the surface of the liquid.

A known weight of salt (equivalent amounts of acid and base) is then shaken with the same quantities of water and benzene (1000 ml. and 60 ml. respectively), and the amount of aniline in the benzene layer determined as above. Instead of using the salt, one may preferably proceed as follows : Shake up 1000 ml. of a solution of hydrogen chloride of known concentration (say 0·1N) with 60 ml. of benzene, in which an amount of aniline equivalent to the hydrochloric acid taken, is contained.

In order to allow for the solubility of benzene in water, and loss by evaporation during the experiment, 1 ml. should be subtracted from the volume of benzene taken, $i.e.$ the total volume of benzene should be taken as 59 ml.

The following results may serve as a comparison [1] :—

Base.	F.	Initial conc. of acid and base.	Weight of hydro-chloride from 50 ml. of benzene solution.		Percentage hydrolysis.
Aniline		0·09969	0·0806	0·00123	1·56
		0·03138	0·0406	0·000621	2·51

[1] See Farmer, *J. Chem. Soc.*, 1901, **79**, 863 ; Farmer and Warth, *ibid.*, 1904, **85**, 1713.

Additional Exercise.—Determine the degree of hydrolysis of sodium ammonium phosphate (Abbott and Bray, *J. Amer. Chem. Soc.*, 1909, **31**, 737).

THE INVESTIGATION OF HOMOGENEOUS EQUILIBRIA.

Determinations of the distribution of a substance between two non-miscible solvents may also be employed for the investigation of other homogeneous equilibria besides those produced by hydrolysis. Thus, one may study the equilibria:[1] $KBr + Br_2 \rightleftharpoons KBr_3$ and $KI + I_2 \rightleftharpoons KI_3$ in aqueous solution.

EXPERIMENT.—*Investigate the equilibrium* $KI + I_2 \rightleftharpoons KI_3$ *in Aqueous Solution.*

One must first determine the distribution coefficient of iodine between water and a suitable non-miscible solvent, such as carbon tetrachloride or carbon disulphide. To do this, prepare a saturated solution of iodine in, say, carbon tetrachloride at the ordinary temperature, and shake up 20 ml. of this solution with 200 ml. of water in a stoppered bottle immersed in the water of a thermostat at 25° (see p. 146). After equilibrium has been attained, allow the bottle to stand in the thermostat for 20–30 minutes so as to secure complete separation of the two liquid layers. The concentration of iodine in the carbon tetrachloride and in the water is then determined by pipetting out a given volume of the solutions (say, 5 ml. of the carbon tetrachloride solution and 50 or 100 ml. of the aqueous solution), and titrating with 0·05N or 0·01N thiosulphate solution. (A small quantity of a concentrated solution of potassium iodide is added to the carbon tetrachloride solution in order to ensure complete extraction of the iodine.) The determination is repeated, using (*a*) 10 ml. of saturated iodine solution, 10 ml. of carbon tetrachloride, and 200 ml. of water; (*b*) 15 ml. of iodine solution, 5 ml. of carbon tetrachloride, and 200 ml. of water. The distribution coefficient is then obtained from the expression $k = \dfrac{\text{concentration in } CCl_4}{\text{concentration in } H_2O}$.

Similar experiments are then carried out using, in place of water, a solution of potassium iodide of known concentration (say 0·1N). The iodine in the two layers is accurately

[1] See Roloff, *Z. physikal. Chem.*, 1894, **13**, 341 ; Jakowkin, *ibid.*, 1896, **20**, 19 ; Dawson, *J. Chem. Soc.*, 1901, **79**, 238.

titrated by means of thiosulphate solution. The concentration of iodine in the two solvents is thereby known. From the concentration of iodine in carbon tetrachloride, the concentration of free iodine in the aqueous solution can be calculated from the distribution coefficient. The titration value of the iodide solution gives the total iodine, and the difference between this and the amount of free iodine gives the iodine combined with potassium iodide to form KI_3. The amount of iodide which has thus combined with iodine can be calculated, and if this amount of iodide is subtracted from the original amount of iodide present, the amount of uncombined iodide is obtained. In this way, the amounts of KI, I_2, and of KI_3 in a given volume of solution can be obtained, and the concentrations calculated. If the equilibrium between KI, I_2, and KI_3 is produced in accordance with the expression $KI + I_2 \rightleftharpoons KI_3$, the equilibrium constant, according to the law of mass action, should be—

$$K = \frac{[KI] \times [I_2]}{[KI_3]}$$

where the square brackets indicate concentrations.

Other reactions which may be studied by means of partition experiments are the reaction between naphthol and picric acid,[1] and the formation of the compound $CuSO_4, 4NH_3$ in aqueous solution.[2]

Preparation of Water free from Carbonic Acid.—Water can be freed from carbonic acid by drawing a current of air, free from carbon dioxide, through the water. The air is purified by passing through a tube containing, first, a layer of calcium chloride, then a layer of soda-lime, and lastly (at end next the water), a layer of cotton-wool. This operation should, of course, be carried out in an atmosphere free from fumes (not in the ordinary laboratory), and the air should preferably be drawn from out-of-doors.

The water is preserved in a flask (preferably of Jena glass) or in a bottle fitted with a siphon tube passing through a closely fitting rubber stopper, or cork protected by paraffin ; and the air which enters into the flask, on withdrawing water, should be made to pass through a tube of soda-lime.

Preparation of Standard Baryta Solutions.—First prepare a clear, saturated solution of barium hydroxide in the follow-

[1] Kuriloff, *Z. physikal. Chem.*, 1898, **25**, 419.
[2] Dawson, *J. Chem. Soc.*, 1906, **89**, 1666.

ing manner. Boil, in a flask, about 250 to 300 ml. of distilled water with excess of barium hydroxide (about 30 to 40 g.), so as to obtain a saturated solution, and then fit into the neck of the flask C (Fig. 66), a cork carrying a soda-lime tube, and a longer glass tube E. At this stage, the tube should be drawn through the cork, so that the lower end does not dip into the solution, and the upper end should be closed by a cap. When the solution becomes cold, the excess of baryta will crystallize out, and will drag down with it the suspension of barium carbonate, leaving a clear solution, which will have a concentration of about 0·4 normal. This solution is then transferred to the stock bottle, A, with which the burette, B, is permanently connected.
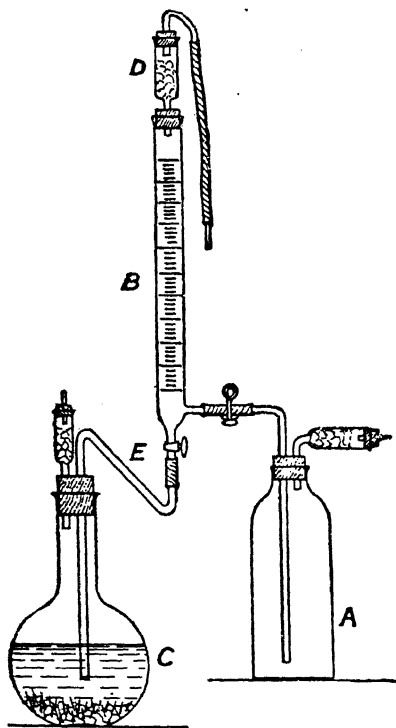
FIG. 66.

The neck of the stock bottle, of about 2 litres capacity, is closed by means of a paraffined cork or by a rubber stopper, bored with two holes. Through one of these there passes the end of a soda-lime tube, and through the other a bent glass tube, one end of which reaches nearly to the bottom of the bottle, while the other end is connected by means of rubber tubing, carrying a spring clip, to the side tube of the burette B. The upper end of the burette is closed by an air-tight cork through which passes a soda-lime tube, D, fitted with rubber tubing carrying a glass mouthpiece.

Having closed the lower end of the burette, attach the soda-lime tube on A to a filter pump, and draw a current of air (freed from carbon dioxide by means of the soda-lime) through the burette and bottle for about 10 minutes. Now

close the tube D and draw into the bottle, through the lower end of the burette, about $1\frac{1}{2}$ litres of distilled water, free from carbon dioxide (p. 153, or the water may be freed from carbon dioxide in this bottle). Connect the end of the tube E with the lower end of the burette ; attach the soda-lime tube on C to a filter-pump, and draw a current of CO_2-free air through D, the tube connecting the burette with the bottle A being meanwhile closed. After the tube E has been freed from carbon dioxide, the current of air is stopped, and the tube E is carefully pushed through the cork until the lower end is just a little above the solid baryta at the bottom of the flask C. Tube D is now closed, the connection between the burette and the bottle A is opened, and the clear solution of baryta is drawn into A. The flask with the baryta is then disconnected from the burette, and the solution in the bottle thoroughly mixed by drawing a current of CO_2-free air through the solution. The solution thus prepared is approximately 0·05 normal. It is best standardized by means of pure succinic acid, phenolphthalein being used as indicator.

CHAPTER X

CONDUCTIVITY OF ELECTROLYTES

WHEN a current of electricity flows through a uniform conductor ab, the *strength* or intensity of the current depends on the *difference of potential* between the two points a and b and the *resistance* of the conductor ; and according to Ohm's law, it is equal to the difference of potential divided by the resistance, *i.e.* $I=E/R$. When the current is measured in *amperes*, the difference of potential in *volts*, and the resistance in *ohms*, one obtains the definition that one ampere is the strength of current produced in a conductor which has a resistance of 1 ohm, and between the ends of which there is a difference of potential of 1 volt.

The unit of electrical energy is 1 volt $\times$ 1 coulomb$=10^7$ ergs ; but the strength of the current, and therefore also the amount of electricity flowing in unit time, depend on the resistance, or on the conductance, which is the reciprocal of the resistance. It will therefore be seen that the amount of energy conveyed through a conductor will depend on the difference of potential between its ends and on its resistance or conductance. The measurement of conductance or resistance may first be considered.

The resistance offered by a regular cube of the conductor having sides 1 cm. long, is called the *specific resistance* or *resistivity* of the material, and the reciprocal of this is called the *specific conductance* or the *conductivity*, and is generally represented by κ. Although a knowledge of the conductivity, whether of a metal or of a liquid conductor, is of importance in physics and electro-technics, it is not, in itself, of so much importance in chemistry or physical chemistry, with which we are here chiefly concerned ; for in the case of conducting solutions, which alone will be dealt with here, the conductance does not depend on the whole of the material between the electrodes, but almost entirely on the solute. When, therefore, it is desired to compare different

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substances with respect to the conductivity which they exhibit in solution, one should compare chemically comparable quantities, *i.e.* equivalent or equi-molecular quantities. In this way one obtains the equivalent conductivity and the molecular conductivity. By *equivalent conductivity* is meant the conductance of a solution which contains 1 gram-equivalent of the solute, when placed between two electrodes of indefinite size and 1 cm. apart. It is represented by Λ, and is numerically equal to the specific conductance (κ) multiplied by the volume in millilitres (ϕ) containing 1 gram-equivalent of solute. That is, $\Lambda = \kappa \cdot \phi = 1000 \, \kappa/c$, where c is the concentration in gram-equivalents per litre.

By *molecular conductivity* is meant the conductance of a solution containing 1 gram-molecule of the solute when placed between two electrodes of indefinite size and 1 cm. apart. It is represented by $\mu = \kappa \cdot \phi'$, where ϕ' is the volume in millilitres containing 1 gram-molecule of the solute.

Outline of Method and Apparatus.[1]—For the purpose of measuring the resistance of a solution, one usually employs the Wheatstone bridge method, the arrangement of which is shown diagrammatically in Fig. 67. Since, during the electrolysis of an aqueous solution between platinum electrodes, gases are evolved, and a back electromotive force (polarization e.m.f.) therefore produced, one
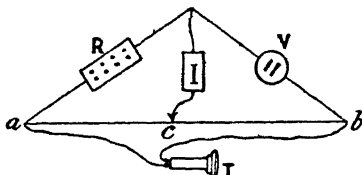
FIG. 67.

cannot readily measure the resistance of a liquid conductor by means of a direct current, but must employ an alternating current represented in Fig. 67 by I. Although, for less exact measurements, a small induction coil may be employed as the source of alternating current, it is rather unsatisfactory and not suitable for use in investigations demanding the highest degree of accuracy. Various other sources of alternating current are now available and of these one of the best and most frequently used is the valve oscillator

[1] For a discussion of the precautions necessary to ensure the highest accuracy in the measurement of the conductivity of liquids, see Morgan and Lammert, *J. Amer. Chem. Soc.*, 1926, **48**, 1220; Jones and Josephs, *ibid.*, 1928, **50**, 1049; Shedlovsky, *ibid.*, 1930 **52**, 1793; Jones and Bradshaw, *ibid.*, 1933, **55**, 1780; Davies, *J. Chem. Soc.*, 1937, 432; Righellato and Davies, *T. Faraday Soc.*, 1933, **29**, 429; Davies, *The Conductivity of Solutions*.

(*v. infra*). A low-resistance telephone,[1] T, is connected to the ends of a wire *ab*, which is made of platinum or platinum-iridium, and is stretched above a scale divided into milli-metres. R is a resistance box and V is a conductivity cell containing the solution to be investigated. A known re-sistance is inserted in R, the resistance being of the same order as that of the liquid in the conductivity cell, and the sliding contact *c* is moved along the wire *ab* until there is silence in the telephone. When this is the case, the resist-ance of V is given by the expression,

$$R : V = ac : cb \; ; \text{ or } V = R \cdot \frac{cb}{ac}$$

Actual silence may not be found at the point of balance, but only a *sound minimum*, and one must therefore take the mean of two points of equal sound in-tensity on either side of the minimum. The sharpness with which the point of balance can be determined depends on various factors, such as the resistance of the solution, the size of the electrodes, their distance apart and the nature of their surface. The point of balance can be determined with greater sharpness by placing a variable air condenser in parallel with the variable resistance R, and so balancing the capacity as well as the resistance of the two sides of the bridge.
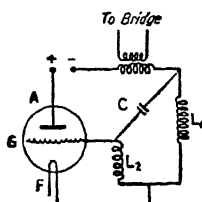
FIG. 68.

Alternating current of suitable frequency, say 1000 cycles per second, can be generated in a number of radio circuits, such as that indicated in Fig. 68. In this figure, L_1 and L_2 are variable inductances and C is a condenser, and by variation of these, the frequency of the oscillations can be varied, the oscillatory circuit being formed of the grid, G, and filament, F, with the inductance and capacity. The purity and uniformity of the oscillations can be im-proved by means of suitable choking coils and filters.[2]

In general, it is necessary to amplify the oscillations by means of a second valve tube.

[1] An improvement consists in using a telephone which can be tuned to resound to the frequency of the alternating current used.

[2] The construction of a valve oscillator from components readily obtain-able for the construction of broadcast receivers is described by Woolcock and Murray-Rust (*Phil. Mag.*, 1928, [vii], **5**, 1130).

Oscillating current of suitable audio-frequency can also be obtained by means of the reed hummer designed by the British Post Office. In this instrument,[1] a tuned reed A (Fig. 69) is fixed near to a permanent magnet D, which has coils wound on its pole tips. A microphone button is attached to the reed. In conjunction with a transformer E, two condensers C_1 and C_2 form a tuned circuit. The reed is made to vibrate and thereby a disturbance is set up in the microphone. This produces a variable current through the magnet coils, which reacts on the reed and maintains it in permanent vibration. In this way an alternating current of, say, 1000 cycles per second is obtained.

In the microphone hummer, the frequency of the alternating current is maintained by means of an electrically controlled tuning fork.

The *resistance box* contains a number of wire resistances, the ends of which are attached to brass blocks on the top of
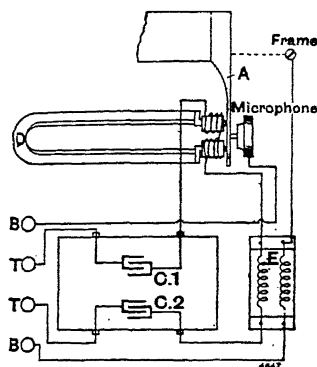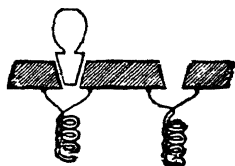
FIG. 69.   FIG. 70.

the box, electrical connection between these being made by means of brass plugs (Fig. 70). By removing the plugs, resistance is placed in the circuit, the current being then made to pass through the wire. The value of the resistance inserted is marked opposite each plug-hole.

Care must be taken that these plugs do not become dirty. When taken out, they should be placed on the top of the box or in the blind holes made for them, and not on the working bench. The plugs should be wiped from time to time with a cloth moistened with light petroleum ; and when the box is not in use, they should all be inserted in their places.

Dial resistance boxes are also much in use. These contain resistances arranged in sets of ten coils, in units,

[1] Supplied by the Cambridge Instrument Co., Ltd.

tens, hundreds and thousands of ohms, and the resistance can be varied by turning the knobs of the different groups (Fig. 71).

The *conductivity vessel* may have various forms, and, for accurate measurements, attention must be paid to certain

OHMS AT 20° C   LOW INDUCTANCE RESISTANCE   EUREKA

CAMBRIDGE
INSTRUMENT Cº LT. —
ENGLAND

Nº L·33965

THOUSANDS   HUNDREDS   TENS   UNITS

ADD ZERO RES ·007Ω
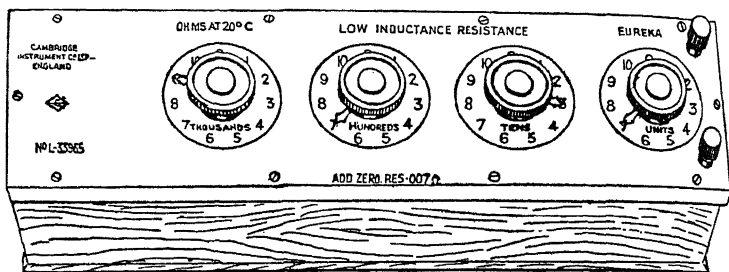
FIG. 71.

details of construction.[1]   For general laboratory purposes, the simple forms of vessel shown in Fig. 72, are very suitable and are widely used.

The conductivity cells, A and B, consist of cylindrical glass vessels, either of uniform diameter or narrowed at the foot, for use with

A   B   C
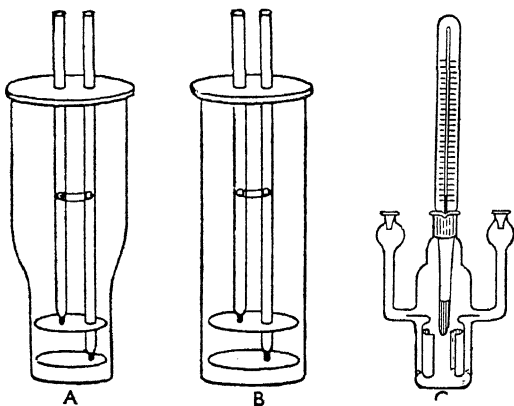
FIG. 72.

liquids of greater conductivity.   The electrodes are circular platinum plates sealed into glass tubes, and electrical connection is made by means of mercury.   These two tubes pass through an ebonite cover,

[1] See C. W. Davies, *J. Chem. Soc.*, **1937**, 432, where references to the literature are given.

and their relative positions must be fixed either by means of a glass tie, or by cementing the tubes to the cover. The cover is also furnished with two holes for the insertion of a thermometer (if desired) and of a pipette (see below). When not in use, these should be closed by means of small corks or rubber plugs. When the cell, c, is used, the thermometer may be replaced by a glass stopper.

The glass vessels are best cleaned and dried by first subjecting them for five or ten minutes to the action of steam, and then drawing a current of air through them by means of a filter pump. A very convenient apparatus for the purpose of steaming out the vessels is shown in Fig. 73. The glass tube T is fitted by means of a piece of rubber tubing into the stem of a funnel which passes through the cork in the neck of the flask F. The vessel to be cleaned is placed over the end of the tube T, and water is boiled in the flask. The steam passes up through the tube, and the condensed steam collects in the funnel.

Platinizing the Electrodes.—The sharpness with which the sound minimum can be determined depends largely on the nature of the surface of the electrodes, and is increased by coating these with platinum black.[1] This is best done electrolytically.

A quantity of platinizing solution (3 g. of platinum chloride, 0·02–0·03 g. of lead acetate, 100 ml. water) is placed in the conductivity vessel, and the electrodes, previously cleaned by means of chromic acid, lowered into the solution. The vessel should be supported in an inclined position, in order to allow the gas which is evolved during electrolysis to escape readily. The elec-

FIG. 73.

trodes are connected with a battery of two lead accumulators (4 volts) through a commutator, which allows of the current being reversed. By means of a sliding resistance the current is regulated so that there is only a moderately rapid evolution of gas. The current should be passed for 10–15 minutes, its direction being reversed every half-minute. The coating should be black and velvety in appearance.

On account of the adsorbing power of platinum black, the removal of the last traces of platinizing liquid and occluded chlorine sometimes causes difficulty. It can best be effected either by placing the electrodes in a solution of sodium acetate or dilute sulphuric acid and passing a current for about a quarter of an hour, with reversal
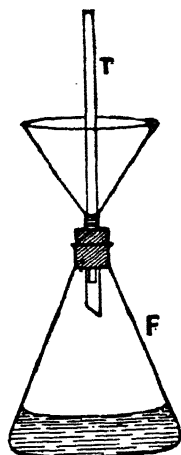
[1] See Jones and Bollinger, *J. Amer. Chem. Soc.*, 1935, **57**, 280. For accurate measurements of the conductance of very dilute solutions, however, platinized electrodes may not be used on account of their power of adsorption. The adsorption is greatly reduced by heating the platinized electrodes to redness (Whetham, *Phil. Trans.*, 1900, **194**, 321).

of the current every minute ; or by connecting the two electrodes
together and making them the cathode in a solution of dilute sul-
phuric acid, another platinum electrode being employed as anode.
In this case the current is, of course, not reversed.

After being treated in this manner, the electrodes are well washed
with warm distilled water, and then several times with conductivity
water (p. 165), until all soluble matter has been removed (see p. 167).

The Measuring Bridge.—This very commonly consists
of a thin wire of platinum, platinum-iridium, or nickelin,
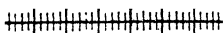
FIG. 74.

stretched over a scale 1 metre long and graduated in milli-
metres (Fig. 74). A sliding contact c, having a platinum
knife-edge, makes contact with the wire. At the end of the
bridge are terminals T, by means of which electrical contact
with the bridge wire can be established.

The position of sound-minimum can be determined most
sharply when the sliding contact is near the end of the bridge
wire ; but, on the other hand, an error in the reading near
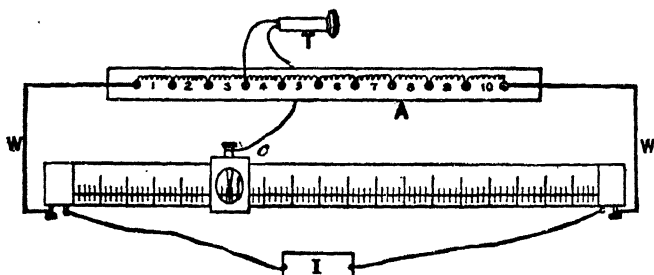
FIG. 75.

the end of the wire has a greater influence on the result than
when the sliding contact is near the middle of the wire. In
order, therefore, to balance the errors of setting and of
reading, it is best so to arrange the resistances in the box
that the position of balance on the bridge wire lies between
20 and 40, or between 60 and 80 cm.

Calibration of the Bridge Wire.—If there is any doubt regarding
its uniformity, the bridge wire should be calibrated before being used.
This is best done by the method of Strouhal and Barus, the arrange-
ment for which is shown diagrammatically in Fig. 75.

The calibration bridge A consists of a strip of wood carrying 11 mercury cups. These cups are connected by 10 approximately equal resistances, the sum of which should be about the same as the total resistance of the bridge wire. These resistances, one of which should be marked differently from the others, are very suitably made of thin manganin wire soldered to thick copper wires, the ends of which, *previously cleaned and amalgamated,*[1] dip into the mercury cups (Fig. 76).

The ends of the calibration bridge are connected by non-resistance wires (thick copper wires), WW, to the ends of the measuring bridge (Fig. 75); and the latter is also connected with the secondary of a small induction coil, I, or other source of alternating current of suitable frequency. The sliding contact c is connected with one terminal of a telephone T, while the other terminal is connected with one or other of the mercury cups.

The connections having been made, and the resistance wires placed in position in the calibration bridge, place the lead from the telephone in the second mercury cup from the left end of the calibration bridge, *i.e.* between the first and second resistances. Move the sliding contact c until the position of sound minimum is obtained (see p. 158). The resistance of this length of the measuring wire, which we shall call a, will evidently bear the same relation to the
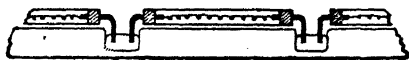
FIG. 76.

total resistance of the wire as the resistance 1 bears to the sum of the ten resistances. Now interchange resistance 1 with resistance 2, the lead from the telephone being still kept in the second mercury cup.[2] Again determine the position of sound minimum, and let this reading be b. The resistance of this length of wire will bear the same relation to the total resistance of the bridge wire as resistance 2 bears to the sum of the ten resistances.

Now move the lead from the telephone into the third mercury cup, and again determine the position of sound minimum. This point, c, on the bridge wire marks off a resistance which bears the same relation to the total resistance as the sum of the resistances 1 and 2 bears to the sum of the ten resistances. By subtracting b from c, a length on the bridge wire is obtained which bears the same relation to the total resistance of the bridge wire as resistance 1 bears

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[1] In all measurements of electrical resistance or conductance, whenever connections have to be made by means of copper wires dipping into mercury, one should invariably make it a rule to see that the ends of the copper wires are rubbed quite clean, and, if necessary, freshly amalgamated.

[2] Since the method of calibration consists in dividing the measuring wire into ten portions of equal resistance, each proportional to the resistance of one of the ten calibration resistances, it is well to have one of the latter specially marked. At the commencement of the calibration, this special resistance must be placed at the extreme left of the calibration bridge; it is the resistance which we have numbered 1.

to the sum of the ten resistances. That is, the resistance of the length $c-b$ is equal to that of a.

Interchange the resistance 1 with resistance 3, and again find the position of sound minimum, with the lead from the telephone still in the third mercury cup. This reading, d, will give a length of wire, the resistance of which bears to the total resistance the same relation as the sum of the resistances 2 and 3 bears to the sum of the ten resistances. Now place the lead from the telephone in cup 4, and find another position of sound minimum, say e. Then it follows, as before, that $e-d$ is equal to a.

The measurements are continued in this way along the bridge until the resistance 1 has successively occupied the place of each of the others, and has reached the right-hand end of the calibration bridge. The last position of sound minimum (in the neighbourhood of 90 cm.) is determined with the lead from the telephone in the tenth mercury cup, and this reading is subtracted from 100 to give the final length of the bridge wire equal to a. By this method, the bridge wire has been divided into 10 equal resistances, each of which is equal, or approximately equal, to one-tenth of the whole resistance.

No. of reading.	Reading on bridge wire.	Length proportional to resistance 1.	Correction to reduce sum of lengths to 100.	Corrected lengths of equal resistance.	Length corresponding to the readings 10, 20, 30, etc., cm. on bridge wire.	Correction in mm. to be applied at the end of each 10 cm.
a	10·05	10·05	−0·04	10·01	10·01	−0·1
b	10·12 }					
c	20·12 }	10·00	−0·04	9·96	19·97	+0·3
d	19·65 }					
e	29·60 }	9·95	−0·04	9·91	29·88	+1·2
f	29·60 }					
g	39·60 }	10·00	−0·04	9·96	39·84	+1·6
h	39·53 }					
i	49·60 }	10·07	−0·04	10·03	49·87	+1·3
j	49·70 }					
k	59·80 }	10·10	−0·04	10·06	59·94	+0·6
l	59·70 }					
m	69·80 }	10·10	−0·04	10·06	70·00	0·0
n	69·73 }					
o	79·73 }	10·00	−0·04	9·96	79·96	+0·4
p	79·95 }					
q	89·92 }	9·97	−0·04	9·93	89·89	+1·1
r	89·95 }					
	100·00 }	10·15	−0·04	10·11	100·00	
		100·39		99·99		

The ten lengths are added together, and the difference of the sum from 100 taken. One-tenth of this difference is then subtracted from (or added to) each of the a values, so that these now add up to 100. The corrected value of a_1 then gives the length correspond-

ing to 10 cm. of the bridge wire; $a_1 + a_2$, that corresponding to 20 cm. of the bridge wire, etc. The differences of a_1, $a_1 + a_2$, etc., from 10, 20, etc., give the corrections to be applied at these points of the bridge wire. The correction to be applied at an intermediate point is obtained by interpolation, which is best carried out graphically as in the case of the calibration of a burette (p. 25).

The table on the previous page, giving the values actually obtained for one wire, will illustrate the foregoing description.

Instead of using an alternating current for calibrating the bridge wire, one may employ a direct current. The connections are the same as those given in the diagram (Fig. 75, p. 162), but the place of the induction coil is taken by a lead, cupron, or other cell, and the telephone is replaced by a galvanometer. A tapping key is inserted in the galvanometer circuit, so that the current can pass through the galvanometer only when the key is depressed. The sliding contact is then moved along the bridge wire until a position is found such that on depressing the tapping key no movement of the galvanometer needle takes place.

Conductivity Water.—On account of the sensitiveness of the conductivity method, it is necessary to use water of a high degree of purity. The purest water which has so far been obtained had a specific conductance of 0.4×10^{-7} mhos (reciprocal ohms) at $18°$; but for most purposes, except those demanding the highest degree of accuracy, water having a conductivity of $2-3 \times 10^{-6}$ mhos will be sufficiently pure. Water having a conductivity greater than 3×10^{-6} mhos should not be used. Various apparatus have been described [1] for the production of water of a high degree of purity, but suitable conductivity water can readily be obtained by distillation, from a glass retort, of ordinary distilled water to which a little potassium permanganate has been added. The distillation must be carried out in an atmosphere free from fumes and best in the open air; and the distillation should not be carried out too rapidly. The condenser is best made of block tin, but a tube of Jena or "resistance" glass can also be used with good results. Only the middle fraction should be retained.

Since water dissolves an appreciable amount of matter from ordinary glass, the flask or bottle in which the conductivity water is stored should either have been thoroughly "seasoned," or should be made of a sparingly soluble glass, e.g. Jena or pyrex glass.

[1] See Bourdillon, *J. Chem. Soc.*, 1913, **103**, 791; Kendall, *J. Amer. Chem. Soc.*, 1916, **38**, 2460; Kraus and Dexter, *ibid.*, 1922, **44**, 2468; Hartley, Campbell and Poole, *J. Chem. Soc.*, 1908, **93**, 428; Thiessen and Heumann, *Z. Electrochem.*, 1937, **43**, 66.

The Cell Constant.—The specific conductance, it has been stated, is the conductance of 1 cm. cube (*not* 1 c.c.) of the material. If, therefore, the electrodes of the conductivity vessel are not exactly 1 sq. cm. in area and 1 cm. apart, the measured resistance or conductance of a solution placed between them will have to be multiplied by a factor, in order to reduce the value to that which would be obtained if the electrodes enclosed between them 1 cm. cube of the liquid. This factor, which depends on the size and shape of the electrodes, and on their distance apart, is known as the *resistance capacity of the cell* or the *cell constant*. It will be evident that if κ is the specific conductance and c the measured conductance, then the cell constant $K = \dfrac{\kappa}{c}$.

The value of the cell constant can be most easily obtained by measuring the conductance c of a liquid of known conductivity. The liquid which is commonly used for this purpose is a solution of potassium chloride of known conductivity. In the following table are given the values, in reciprocal ohms, of the conductivity of solutions containing 0·1 and 0·01 gram-equivalent (1 gram-equivalent=74·553 g.) of potassium chloride in one *cubic decimetre* (0·999973 litre). These solutions contain 7·4789 and 0·74625 g. of KCl in 1000 g. of water,[1] all weights being corrected for the buoyancy of the air (p. 19).

Temperature.	Conductivity.	
	0·1N	0·01N
0°	0·007138	0·0007736
18°	0·011167	0·0012205
25°	0·012856	0·0014088

EXPERIMENT.—*Determine the Cell Constant of the given Cell.*

Fit up a thermostat and regulate its temperature to 25·0°. Since the temperature has a great influence on the conductivity of a solution, viz. about 2 per cent. per degree, the thermostat must be regulated so that the fluctuation of temperature does not exceed 0·05°–0·1°. Arrange the apparatus

[1] Jones and Bradshaw, *J. Amer. Chem. Soc.*, 1933, **55**, 1780. See also, Jones and Prendergast, *ibid.*, 1937, **59**, 731.

as shown in the diagram (Fig. 67, p. 157). All connections should be made with fairly thick insulated copper wire, so as to have a negligible resistance; and the ends of the wires, where they are attached to metal terminals, must be scraped or rubbed clean with a knife or emery-paper, and where they make contact with mercury (at the conductivity vessel) they must be amalgamated.

The conductivity cell V is best supported in the thermostat by means of a holder such as is shown in Fig. 77. It consists of a plate of brass in which a hole is cut large enough to allow the conductivity cell to pass through, the
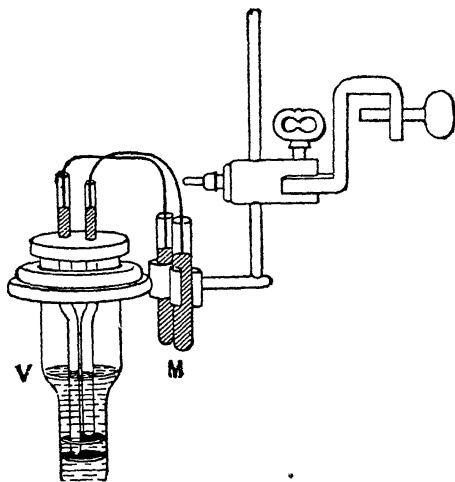
FIG. 77.

cell being supported by means of a thick rubber ring. Electrical connection between the electrodes and the rest of the apparatus is made by means of fairly stout copper wires, the ends of which (amalgamated) dip, on the one hand, into the mercury in the glass tubes which carry the electrodes, and on the other hand, into two small mercury cups, M, attached to the holder. Into these cups the amalgamated ends of the wires leading to the resistance box and to the bridge wire also dip.

If the electrodes have been freshly platinized, it is necessary, before proceeding to make a measurement, to make sure that they have been completely freed from soluble substances by determining the resistance of the conductivity

water in the cell. If any soluble matter remains in the electrodes it will gradually pass into solution, and thus impart a greater conductivity to the water in the cell; and as the soluble matter is removed, the conductance of the water will diminish, or the resistance will increase. The electrodes must therefore be washed for such a time that they no longer affect the conductivity of the water. Sufficient water is placed in the cell to cover the electrodes to a depth at least equal to the distance between the two electrodes, and care is taken that no air-bubbles are enclosed between the electrodes.[1] When the water has taken the temperature of the bath, say after 7–10 minutes, insert a resistance of about 10,000 ohms in the resistance box and determine the position of minimum sound on the bridge wire. Empty the cell, and fill it with another sample of the conductivity water, and again determine the resistance in the above manner. If the electrodes were not quite clean, the resistance should now be found greater than before. Again wash out the cell, and determine the resistance of a fresh portion of the conductivity water; and repeat the operation until a constant value for the resistance of two successive portions of the water is obtained. Owing to the high resistance measured, it will probably be found that the minimum is somewhat indistinct. Several determinations of the minimum position should therefore be made, and the resistance of the water can be taken as constant when the readings on the bridge wire for successive portions of the water do not differ by more than 2–3 mm. Make a note of this reading.

Having in this way made sure that the electrodes are clean, the cell and electrodes are rinsed several times with a standard solution of pure potassium chloride. A quantity of the solution is then placed in the cell, and allowed to take the temperature of the thermostat. The resistance of the solution is then determined by inserting a certain resistance in the box, and determining the position of sound minimum on the bridge wire. Keeping in view what was said regarding the accuracy of the readings on the bridge wire (p. 162), the resistance inserted in the box should be so regulated that

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[1] If the electrodes have been allowed to become dry, it is sometimes found that they are not readily moistened. When this is so, first wash the electrodes with alcohol and then rinse in water. It should be made a rule to keep the electrodes, when not in use, in distilled water.

the readings lie on the middle third of the bridge wire, *i.e.* between the marks 30 and 70 cm.

Several determinations of the resistance of the same sample of solution should be made with different resistances inserted in the box, and in each case several determinations of the position of the sound minimum made. The cell is then filled with a fresh sample of the solution, and again several determinations of the resistance made, in the manner just described. The value of the cell constant is then calculated from each determination of the resistance, and the mean of the different values taken.

The value of the cell constant is calculated as follows : If R is the resistance inserted in the box, and if the sliding contact at the position of balance divides the bridge wire in the ratio $x : 100-x$, where x is the bridge reading in centimetres, then the resistance, R', of the solution is given by $R' = \dfrac{R \cdot (100-x)}{x}$. Hence, the conductance, c', of the solution is $c' = \dfrac{1}{R'} = \dfrac{x}{R \cdot (100-x)}$. If κ denote the specific conductance (conductivity) of the solution (p. 156), then the cell constant, K, is given by the expression—

$$K = \frac{\kappa \cdot (100-x)R}{x}$$

The value of the cell constant having been obtained, the conductivity of the water can be calculated from the determinations of the resistance made above.

If the resistance inserted in the box was R ohms, and if the bridge reading at balance was x cm., then the conductance c' is equal to $\dfrac{x}{R(100-x)}$. But if K is the cell constant, the conductivity, κ, of the water is given by $\kappa = K \cdot c' = \dfrac{K}{R} \cdot \dfrac{x}{(100-x)}$.

The values of the fraction $\dfrac{x}{100-x}$, for values of x from 0·1–99·9 cm., can be obtained from the following table compiled by Obach :—

TABLES OF VALUES OF $\frac{x}{100-x}$, FOR $x=0\cdot1-99\cdot9$ cm.

z	0·0	0·1	0·2	0·3	0·4	0·5	0·6	0·7	0·8	0·9
0	0·0000	0010	0020	0030	0040	0050	0060	0071	0081	0091
1	0101	0111	0122	0132	0142	0152	0163	0173	0183	0194
2	0204	0215	0225	0235	0246	0256	0267	0278	0288	0299
3	0309	0320	0331	0341	0352	0363	0373	0384	0395	0406
4	0417	0428	0438	0449	0460	0471	0482	0493	0504	0515
5	0526	0537	0549	0560	0571	0582	0593	0605	0616	0627
6	0638	0650	0661	0672	0684	0695	0707	0718	0730	0741
7	0753	0764	0776	0788	0799	0811	0823	0834	0846	0858
8	0870	0881	0893	0905	0917	0929	0941	0953	0965	0977
9	0989	1001	1013	1025	1038	1050	1062	1074	1087	1099
10	0·1111	1124	1136	1148	1161	1173	1186	1198	1211	1223
11	1236	1249	1261	1274	1287	1299	1312	1325	1338	1351
12	1364	1377	1390	1403	1416	1429	1442	1455	1468	1481
13	1494	1508	1521	1534	1547	1561	1574	1588	1601	1614
14	1628	1641	1655	1669	1682	1696	1710	1723	1737	1751
15	1765	1779	1793	1806	1820	1834	1848	1862	1877	1891
16	1905	1919	1933	1947	1962	1976	1990	2005	2019	2034
17	2048	2063	2077	2092	2107	2121	2136	2151	2166	2180
18	2195	2210	2225	2240	2255	2270	2285	2300	2315	2331
19	2346	2361	2376	2392	2407	2422	2438	2453	2469	2484
20	0·2500	2516	2531	2547	2563	2579	2595	2610	2626	2642
21	2658	2674	2690	2707	2723	2739	2755	2771	2788	2804
22	2821	2837	2854	2870	2887	2903	2920	2937	2953	2970
23	2987	3004	3021	3038	3055	3072	3089	3106	3123	3141
24	3158	3175	3193	3210	3228	3245	3263	3280	3298	3316
25	3333	3351	3369	3387	3405	3423	3441	3459	3477	3495
26	3514	3532	3550	3569	3587	3605	3624	3643	3661	3680
27	3699	3717	3736	3755	3774	3793	3812	3831	3850	3870
28	3889	3908	3928	3947	3967	3986	4006	4025	4045	4065
29	4085	4104	4124	4144	4164	4184	4205	4225	4245	4265
30	0·4286	4306	4327	4347	4368	4389	4409	4430	4451	4472
31	4493	4514	4535	4556	4577	4599	4620	4641	4663	4684
32	4706	4728	4749	4771	4793	4815	4837	4859	4881	4903
33	4925	4948	4970	4993	5015	5038	5060	5083	5106	5129
34	5152	5175	5198	5221	5244	5267	5291	5314	5337	5361
35	5385	5408	5432	5456	5480	5504	5528	5552	5576	5601
36	5625	5650	5674	5699	5723	5748	5773	5798	5823	5848
37	5873	5898	5924	5949	5974	6000	6026	6051	6077	6103
38	6129	6155	6181	6208	6234	6260	6287	6313	6340	6367
39	6393	6420	6447	6475	6502	6529	6556	6584	6611	6639

s	0·0	0·1	0·2	0·3	0·4	0·5	0·6	0·7	0·8	0·9
40	0·6667	6695	6722	6750	6779	6807	6835	6863	6892	6921
41	6949	6978	7007	7036	7065	7094	7123	7153	7182	7212
42	7241	7271	7301	7331	7361	7391	7422	7452	7483	7513
43	7544	7575	7606	7637	7668	7699	7731	7762	7794	7825
44	7857	7889	7921	7953	7986	8018	8051	8083	8116	8149
45	8182	8215	8248	8282	8315	8349	8382	8416	8450	8484
46	8519	8553	8587	8622	8657	8692	8727	8762	8797	8832
47	8868	8904	8939	8975	9011	9048	9084	9121	9157	9194
48	9231	9268	9305	9342	9380	9418	9455	9493	9531	9570
49	9608	9646	9685	9724	9763	9802	9841	9881	9920	9960
50	1·000	1·004	1·008	1·012	1·016	1·020	1·024	1·028	1·033	1·037
51	1·041	1·045	1·049	1·053	1·058	1·062	1·066	1·070	1·075	1·079
52	1·083	1·088	1·092	1·096	1·101	1·105	1·110	1·114	1·119	1·123
53	1·128	1·132	1·137	1·141	1·146	1·151	1·155	1·160	1·165	1·169
54	1·174	1·179	1·183	1·188	1·193	1·198	1·203	1·208	1·212	1·217
55	1·222	1·227	1·232	1·237	1·242	1·247	1·252	1·257	1·262	1·268
56	1·273	1·278	1·283	1·288	1·294	1·299	1·304	1·309	1·315	1·320
57	1.326	1·331	1·336	1·342	1·347	1·353	1·358	1·364	1·370	1·375
58	1·381	1·387	1·392	1·398	1·404	1·410	1·415	1·421	1·427	1·433
59	1·439	1·445	1·451	1·457	1·463	1·469	1·475	1·481	1·488	1·494
60	1·500	1·506	1·513	1·519	1·525	1·532	1·538	1·545	1·551	1·558
61	1·564	1·571	1·577	1·584	1·591	1·597	1·604	1·611	1·618	1·625
62	1·632	1·639	1·646	1·653	1·660	1·667	1·674	1·681	1·688	1·695
63	1·703	1·710	1·717	1·725	1·732	1·740	1·747	1·755	1·762	1·770
64	1·778	1·786	1·793	1·801	1·809	1·817	1·825	1·833	1·841	1·849
65	1·857	1·865	1·874	1·882	1·890	1·899	1·907	1·915	1·924	1·933
66	1·941	1·950	1·959	1·967	1·976	1·985	1·994	2·003	2·012	2·021
77	2·030	2·040	2·049	2·058	2·067	2·077	2·086	2·096	2·106	2·115
68	2·125	2·135	2·145	2·155	2·165	2·175	2·185	2·195	2·205	2·215
69	2·226	2·236	2·247	2·257	2·268	2·279	2·289	2·300	2·311	2·322
70	2·333	2·344	2·356	2·367	2·378	2·390	2·401	2·413	2·425	2·436
71	2·448	2·460	2·472	2·484	2·497	2·509	2·521	2 534	2·546	2·559
72	2·571	2·584	2·597	2·610	2·623	2·636	2·650	2·663	2·676	2·690
73	2·704	2·717	2·731	2·745	2·759	2·774	2·788	2·802	2·817	2·831
74	2·846	2·861	2·876	2·891	2·906	2·922	2·937	2·953	2·968	2·984
75	3·000	3·016	3·032	3·049	3·065	3·082	3·098	3·115	3·132	3·149
76	3·167	3·184	3·202	3·219	3·237	3·255	3·274	3·292	3·310	3·329
77	3·348	3·367	3·386	3·405	3·425	3·444	3·464	3·484	3·505	3·525
78	3·545	3·566	3·587	3·608	3·630	3·651	3·673	3·695	3·717	3·739
79	3·762	3·785	3·808	3·831	3·854	3·878	3·902	3·926	3·950	3·975
80	4·000	4·025	4·051	4·076	4·102	4·128	4·155	4·181	4·208	4·236
81	4·263	4·291	4·319	4·348	4·376	4·405	4·435	4·465	4·495	4·525
82	4·556	4 587	4·618	4·650	4·682	4·714	4·747	4·780	4·814	4·848
83	4·882	4·917	4·952	4·988	5·024	5·061	5·098	5·135	5·173	5·211
84	5·250	5·289	5·329	5·369	5·410	5·452	5·494	5·536	5·579	5·623

z	0·0	0·1	0·2	0·3	0·4	0·5	0·6	0·7	0·8	0·9
85	5·667	5·711	5·757	5·803	5·849	5·897	5·944	5·993	6·042	6·092
86	6·143	6·194	6·246	6·299	6·353	6·407	6·463	6·519	6·576	6·634
87	6·692	6·752	6·813	6·874	6·937	7·000	7·065	7·130	7·197	7·264
88	7·333	7·403	7·475	7·547	7·621	7·696	7·772	7·850	7·929	8·009
89	8·091	8·174	8·259	8·346	8·524	8·524	8·615	8·709	8·804	8·901
90	9·000	9·101	9·204	9·309	9·417	9·526	9·638	9·753	9·870	9·989
91	10·11	10·33	10·36	10·49	10·63	10·77	10·90	11·05	11·20	11·35
92	11·50	11·66	11·82	11·99	12·16	12·33	12·51	12·70	12·89	13·08
93	13·29	13·49	13·71	13·93	14·15	14·38	14·63	14·87	15·12	15·39
94	15·67	15·95	16·24	16·54	16·86	17·18	17·52	17·87	18·23	18·61
95	19·00	19·41	19·83	20·28	20·74	21·22	21·73	22·26	22·81	23·39
96	24·00	24·64	25·32	26·03	26·78	27·57	28·41	29·30	30·25	31·26
97	32·33	33·48	34·71	36·04	37·46	39·00	40·67	42·48	44·45	46·62
98	49·00	51·6	54·6	57·8	61·5	70·4	70·4	75·9	82·3	89·9
99	99·0	110	124	142	166	199	249	332	499	999

EXPERIMENT.—*Determine the Equivalent Conductivity and the Dissociation Constant of a weak Acid.*

The apparatus remains the same as in the preceding experiment. Prepare 100 ml. of an N/16 solution of the pure acid.[1] If the latter cannot be weighed, *e.g.* acetic acid, the concentration of the solution must be determined by titration with a standard solution of baryta (p. 153), using phenolphthalein as indicator. Further, two pipettes must be obtained and calibrated, one to *deliver*, the other to *take up* 10 ml. (p. 23).[2] When not in use, these pipettes should be placed in an upright position, with their ends resting on filter paper.

Into the clean, dry conductivity vessel, fixed in the thermostat, introduce 20 ml. of the acid solution with the delivery pipette, and after the solution has taken the temperature of the bath, determine the resistance of the solution, as described in the preceding experiment; readings being taken, as before, with three different resistances in the box.

Having taken a set of readings for the resistance of the solution, withdraw 10 ml. of the solution with the with-

[1] Suitable acids for this experiment are acetic acid, succinic acid, benzoic acid, mandelic acid. Weak polybasic acids (*e.g.* succinic acid), in the dilutions employed here, act electrolytically as monobasic acids, *i.e.* only one hydrogen atom is ionised.

[2] In determinations of the equivalent conductivity, all concentrations should, strictly, be made in terms of gram-equivalents per cm.[3], not per ml. The error involved, however, may be neglected except when a high degree of accuracy is aimed at.

drawal pipette, and introduce 10 ml. of conductivity water with the delivery pipette ; [1] mix the solution well by moving the electrodes up and down, but be careful not to deform the electrodes or to alter their relative positions, and also see that no air-bubbles are enclosed between them. After having determined the resistance of this second solution, which is only half as concentrated as the first, in the same manner as before, again withdraw 10 ml. of the solution and add 10 ml. of water. Determine the resistance of this third solution. Proceed in this manner until the dilution reached is 1024 litres (*i.e.* 1 gram-equivalent in 1024 litres).

The results obtained should be controlled by a second series of determinations, carried out in the same manner with a fresh portion of the initial solution.

In order not to introduce carbon dioxide into the solution from the breath, it is better not to expel the last drop of water from the pipette by blowing, but by closing the upper end of the pipette with the finger and grasping the bulb of the pipette in the hand. The expansion of the air then forces the liquid out of the pipette. If, however, the other method is preferred, then a soda-lime tube must be attached to the end of the pipette.

Calculation.—The specific conductance, κ, of the solution is given, as we have seen, by $\kappa = \dfrac{K}{R} \cdot \dfrac{x}{100-x}$, and the equivalent conductivity is equal to 1000 κ/c, where c is the concentration of the solute in g.-equiv. per litre. Hence, the equivalent conductivity in reciprocal ohms is given by $\Lambda = 1000\ \kappa/c = \dfrac{1000K}{c \cdot R} \cdot \dfrac{x}{100-x}$. The value of the fraction $x/100-x$ can be obtained from the table, p. 170.

Arrange results under the headings c, R, x, Λ, and plot the values of the equivalent conductivity against the concentration.

Degree of Ionization and Ionization Constant.—Since the conductivity of a solution depends on the concentration of the ions, the degree to which a dissolved electrolyte is ionized can be determined from the conductivity of the solution. If the equivalent conductivity at concentration c is represented by Λ_c, and that at zero concentration (infinite dilution) [2] by Λ_0, then the degree of ionization, a, is given by

[1] A sufficient quantity (say 100–200 ml.) of water should be kept in a stoppered flask in the thermostat, so that there need be no delay in waiting for the solutions to take the temperature of the bath after addition of water.

[2] Infinite dilution (or zero concentration), it may be recalled, is the dilution beyond which further dilution has no influence on the equivalent conductivity.

$a = \Lambda_c/\Lambda_0$. If, therefore, the value of Λ_0 [1] is known, and if one determines, in the manner described, the value of Λ_c, the value of a can be calculated.

In the case of weak binary electrolytes, it was shown by Ostwald that the equilibrium between un-ionized molecules and ions obeys the law of mass action. If, therefore, a is the degree of ionization, $(1-a)$ will represent the un-ionized portion. If v is the volume in litres containing 1 g.-equiv., the application of the law of mass action gives (since $a v$ and $(1-a)/v$ represent the concentrations of ions and un-ionized molecules respectively) the expression, $K = a^2/(1-a)v$. K is the dissociation or ionization constant, or, in the case of acids and alkalis, the so-called affinity constant.

Calculation.—*From the values of Λ_c obtained above, calculate the degree of ionization and the ionization constant of the acid investigated.*

In making this calculation use may be made of the following values of Λ_0 (for the temperature of $25°$). The values of K are added for comparison :—

Acid.	Λ_0	K
Acetic acid	390·8	$1·813 \times 10^{-5}$
Succinic acid	382	$6·65 \times 10^{-5}$
Benzoic acid	383	$6·15 \times 10^{-5}$
Mandelic acid	378	$4·17 \times 10^{-4}$

The calculation of the dissociation constant from the values of a is facilitated by the following table [2] :

[1] In the case of weak electrolytes, the equivalent conductivity at zero concentration cannot be determined directly, but must be calculated from the sum of the ionic conductivities.

[2] The position of the decimal point will be easily decided with the help of the following table of values of a and corresponding values of $a^2/1-a$.

a	$\dfrac{a^2}{1-a}$
0·0100	0·0001010
0·0312	0·001005
0·0952	0·01002
0·271	0·1007
0·691	1·006
0·917	10·13
0·991	109·1

Suppose, for example, that a has been found equal to 0·451. On looking up the table for the value of $a^2/1-a$ corresponding to this, we find the number 3705. From the above table we see that, for all values of a between 0·271 and 0·691, the values of $a^2/1-a$ lie between 0·1 and 1·0. Hence, the value of $a^2/1-a$ corresponding to the value of $a = 0·451$, is 0·3705.

TABLE OF VALUES OF $\dfrac{a^x}{1-a}$, FOR VALUES OF a FROM 0·0100–0·999.

a	0	1	2	3	4	5	6	7	8	9
0·010	1010	1030	1051	1072	1093	1114	1136	1157	1179	1201
011	1223	1246	1268	1291	1315	1337	1361	1385	1408	1433
012	1457	1482	1507	1532	1557	1582	1608	1633	1659	1686
013	1712	1739	1765	1792	1820	1847	1875	1903	1931	1959
014	1987	2016	2045	2074	2104	2133	2163	2193	2223	2253
015	2284	2314	2345	2376	2408	2440	2473	2505	2537	2569
016	2602	2635	2668	2706	2734	2768	2802	2836	2871	2905
017	2940	2975	3010	3046	3081	3118	3154	3190	3226	3262
018	3299	3336	3373	3411	3449	3487	3525	3563	3602	3641
019	3680	3719	3758	3798	3838	3878	3918	3958	3999	4040
0·020	4082	4123	4164	4206	4248	4290	4333	4376	4418	4461
021	4505	4548	4591	4635	4680	4724	4759	4813	4858	4903
022	4949	4994	5041	5087	5133	5179	5226	5273	5320	5367
023	5415	5462	5510	5558	5607	5655	5704	5753	5802	5852
024	5902	5952	6002	6052	6103	6154	6204	6256	6307	6358
025	6410	6462	6514	6567	6619	6672	6725	6778	6832	6886
026	6940	6995	7049	7104	7159	7213	7269	7324	7380	7436
027	7492	7548	7605	7662	7719	7777	7834	7892	7949	8007
028	8066	8124	8183	8242	8301	8360	8420	8478	8538	8599
029	8661	8721	8782	8844	8905	8966	9028	9090	9152	9215
0·030	9278	9341	9404	9467	9531	9595	9659	9723	9788	9852
031	9917	9982	1005	1011	1017	1025	1031	1038	1044	1051
032	1057	1063	1070	1077	1084	1091	1098	1104	1111	1118
033	1125	1132	1138	1146	1153	1160	1167	1174	1181	1188
034	1196	1204	1212	1219	1226	1233	1241	1248	1255	1263
035	1270	1277	1285	1292	1300	1307	1314	1322	1330	1337
036	1345	1352	1360	1368	1375	1383	1391	1398	1406	1414
037	1422	1430	1438	1446	1454	1462	1470	1478	1486	1494
038	1502	1510	1518	1526	1534	1543	1551	1559	1567	1575
039	1583	1592	1600	1608	1616	1625	1633	1642	1650	1658
0·040	1667	1675	1684	1692	1701	1710	1718	1727	1736	1744
041	1753	1762	1770	1779	1788	1797	1805	1814	1823	1832
042	1841	1850	1859	1868	1877	1886	1895	1904	1913	1922
043	1932	1941	1950	1959	1968	1978	1987	1996	2005	2015
044	2024	2034	2043	2053	2062	2071	2081	2090	2100	2110
045	2119	2129	2139	2149	2159	2168	2178	2188	2198	2208
046	2217	2227	2237	2247	2257	2267	2277	2287	2297	2307
047	2317	2327	2337	2347	2357	2368	2379	2389	2399	2409
048	2420	2430	2440	2450	2461	2471	2482	2492	2503	2513
049	2524	2534	2545	2555	2566	2577	2587	2599	2610	2620
0·050	2631	2642	2653	2663	2674	2685	2696	2707	2718	2729
051	2741	2752	2763	2774	2785	2796	2807	2818	2829	2840
052	2852	2863	2874	2885	2897	2908	2919	2931	2942	2953
053	2965	2977	2989	3000	3012	3023	3035	3047	3058	3070
054	3081	3093	3105	3116	3128	3140	3152	3164	3176	3187

a	0	1	2	3	4	5	6	7	8	9
0·055	3199	3211	3223	3235	3248	3260	3272	3284	3296	3308
056	3321	3333	3345	3357	3370	3383	3395	3407	3419	3432
057	3444	3457	3469	3481	3494	3507	3520	3532	3545	3558
058	3570	3583	3595	3608	3621	3634	3647	3660	3673	3686
059	3699	3711	3724	3737	3751	3764	3777	3790	3803	3816
0·060	3830	3843	3856	3870	3883	3896	3910	3923	3936	3950
061	3963	3977	3990	4004	4017	4030	4044	4057	4071	4084
062	4098	4111	4125	4139	4153	4166	4180	4194	4208	4222
063	4236	4250	4264	4278	4292	4306	4320	4334	4348	4362
064	4376	4391	4405	4419	4434	4448	4462	4477	4491	4505
065	4519	4534	4548	4563	4577	4592	4606	4621	4635	4650
066	4664	4679	4694	4708	4723	4738	4752	4767	4782	4796
067	4811	4826	4841	4856	4871	4886	4901	4916	4931	4946
068	4961	4976	4992	5007	5023	5038	5054	5069	5085	5100
069	5115	5130	5146	5161	5177	5192	5208	5223	5239	5254
0·070	5269	5284	5300	5316	5331	5347	5362	5378	5394	5410
071	5426	5442	5458	5474	5490	5506	5522	5538	5554	5570
072	5586	5602	5619	5636	5652	5668	5685	5701	5717	5733
073	5749	5766	5782	5799	5815	5832	5848	5865	5881	5898
074	5914	5931	5947	5964	5981	5997	6014	6031	6047	6064
075	6081	6098	6115	6132	6149	6166	6183	6200	6217	6234
076	6251	6268	6286	6303	6320	6338	6355	6372	6390	6407
077	6424	6442	6459	6477	6494	6512	6529	6547	6564	6582
078	6599	6617	6634	6652	6670	6687	6705	6723	6740	6758
079	6776	6794	6812	6829	6847	6865	6883	6901	6919	6937
0·080	6955	6973	6992	7010	7029	7047	7066	7084	7103	7121
081	7139	7158	7176	7197	7215	7234	7252	7270	7288	7307
082	7325	7344	7362	7381	7400	7418	7437	7456	7474	7495
083	7513	7532	7551	7570	7589	7608	7627	7646	7665	7684
084	7703	7722	7741	7761	7780	7799	7819	7838	7857	7876
085	7896	7916	7935	7955	7975	7994	8014	8033	8053	8072
086	8092	8112	8131	8151	8171	8190	8210	8230	8250	8270
087	8290	8310	8330	8350	8370	8391	8411	8431	8451	8471
088	8491	8511	8532	8552	8572	8593	8613	8633	8654	8674
089	8695	8715	8736	8757	8777	8798	8819	8839	8860	8881
0·090	8901	8922	8942	8963	8984	9005	9026	9047	9068	9089
091	9110	9131	9152	9173	9195	9216	9237	9258	9280	9301
092	9322	9343	9365	9386	9408	9429	9451	9472	9494	9515
093	9536	9557	9579	9601	9622	9644	9666	9687	9709	9731
094	9753	9775	9796	9818	9840	9862	9884	9906	9928	9950
095	9972	9994	1002	1004	1006	1008	1011	1013	1015	1017
096	1020	1022	1024	1027	1029	1031	1033	1036	1038	1040
097	1042	1044	1047	1049	1051	1054	1056	1058	1060	1063
098	1065	1067	1069	1072	1074	1076	1079	1081	1083	1086
099	1088	1090	1092	1095	1097	1099	1101	1104	1106	1109

	0	1	2	3	4	5	6	7	8	9
0·10	1111	1135	1159	1183	1207	1232	1257	1282	1308	1333
11	1360	1386	1413	1440	1467	1494	1522	1550	1579	1607
12	1636	1666	1695	1725	1755	1786	1817	1848	1879	1911
13	1943	1975	2007	2040	2073	2107	2141	2175	2209	2244
14	2279	2314	2350	2386	2422	2459	2496	2533	2571	2609
15	2647	2686	2725	2764	2803	2843	2883	2924	2965	3006
16	3048	3090	3132	3174	3217	3261	3304	3348	3392	3437
17	3482	3527	3573	3619	3665	3712	3759	3807	3855	3903
18	3951	4000	4049	4099	4149	4199	4250	4301	4353	4403
19	4457	4509	4562	4616	4670	4724	4778	4833	4888	4944
0·20	5000	5056	5113	5171	5228	5286	5345	5403	5463	5522
21	5582	5643	5704	5765	5826	5889	5951	6014	6077	6141
22	6205	6270	6335	6400	6466	6532	6599	6666	6734	6802
23	6870	6939	7008	7078	7148	7219	7290	7362	7434	7506
24	7579	7652	7726	7800	7875	7950	8026	8102	8179	8256
25	8333	8411	8490	8569	8648	8728	8809	8890	8971	9053
26	9135	9218	9301	9385	9470	9554	9640	9726	9812	9899
27	9986	1007	1016	1025	1034	1043	1052	1061	1070	1080
28	1089	1099	1108	1117	1127	1136	1146	1155	1165	1175
29	1185	1194	1204	1214	1224	1234	1245	1255	1265	1275
0·30	1286	1296	1307	1317	1328	1339	1349	1360	1371	1382
31	1393	1404	1415	1426	1437	1449	1460	1471	1483	1494
32	1506	1518	1529	1541	1553	1565	1577	1589	1601	1613
33	1625	1638	1650	1663	1675	1688	1700	1713	1726	1739
34	1752	1765	1778	1791	1804	1817	1831	1844	1857	1871
35	1885	1898	1912	1926	1940	1954	1968	1982	1996	2011
36	2025	2040	2054	2068	2083	2098	2113	2128	2143	2158
37	2173	2188	2203	2219	2234	2250	2266	2281	2297	2313
38	2329	2345	2361	2378	2394	2410	2427	2443	2460	2477
39	2493	2510	2527	2545	2562	2579	2596	2614	2631	2649
0·40	2667	2685	2702	2720	2739	2757	2775	2793	2812	2830
41	2849	2868	2887	2906	2925	2944	2963	2983	3002	3022
42	3041	3061	3081	3101	3121	3141	3162	3182	3203	3223
43	3244	3265	3286	3307	3328	3349	3371	3392	3414	3435
44	3457	3479	3501	3523	3546	3568	3591	3613	3636	3659
45	3682	3705	3728	3752	3775	3799	3822	3846	3870	3894
46	3919	3943	3967	3992	4017	4042	4067	4092	4117	4142
47	4168	4194	4219	4245	4271	4298	4324	4351	4377	4404
48	4431	4458	4485	4512	4540	4568	4595	4613	4651	4680
49	4708	4736	4765	4794	4823	4852	4881	4911	4940	4970
0·50	5000	5030	5060	5091	5121	5152	5183	5214	5245	5277
51	5308	5340	5372	5404	5436	5469	5501	5534	5567	5600
52	5633	5667	5701	5734	5768	5803	5837	5871	5906	5941
53	5977	6012	6048	6083	6119	6155	6192	6228	6265	6302
54	6339	6377	6414	6452	6490	6528	6566	6605	6644	6683

a	0	1	2	3	4	5	6	7	8	9
0·55	6722	6762	6801	6841	6882	6922	6963	7003	7044	7086
56	7127	7169	7211	7253	7296	7339	7382	7425	7468	7512
57	7556	7600	7645	7689	7734	7779	7825	7871	7917	7963
58	8010	8056	8103	8151	8199	8246	8295	8343	8392	8441
59	8490	8540	8590	8640	8691	8741	8792	8844	8896	8948
0·60	9000	9053	9106	9159	9213	9267	9321	9375	9430	9485
61	9541	9597	9653	9710	9767	9824	9882	9940	9998	1006
62	1012	1018	1024	1030	1036	1042	1048	1054	1060	1066
63	1073	1079	1085	1092	1098	1105	1111	1118	1124	1131
64	1138	1145	1151	1158	1165	1172	1179	1186	1193	1200
65	1207	1214	1222	1229	1236	1244	1251	1258	1266	1274
66	1281	1289	1297	1304	1312	1320	1328	1336	1344	1352
67	1360	1369	1377	1385	1393	1402	1410	1419	1428	1436
68	1445	1454	1463	1473	1482	1491	1499	1508	1517	1526
69	1536	1545	1555	1564	1574	1583	1593	1603	1613	1623
0·70	1633	1643	1654	1664	1674	1685	1695	1706	1717	1727
71	1738	1749	1760	1771	1783	1794	1805	1817	1828	1840
72	1851	1863	1875	1887	1899	1911	1924	1936	1949	1961
73	1974	1987	1999	2012	2025	2039	2052	2065	2079	2092
74	2106	2120	2134	2148	2162	2177	2191	2206	2220	2235
75	2250	2265	2280	2296	2311	2327	2342	2358	2374	2390
76	2407	2423	2440	2456	2473	2490	2508	2525	2542	2560
77	2578	2596	2614	2632	2651	2669	2688	2707	2727	2746
78	2766	2785	2805	2825	2846	2866	2887	2908	2929	2950
79	2972	2994	3016	3038	3060	3083	3106	3129	3153	3176
0·80	3200	3224	3249	3273	3298	3323	3348	3374	3400	3427
81	3453	3480	3507	3535	3562	3590	3619	3648	3677	3706
82	3736	3766	3796	3827	3858	3889	3921	3953	3986	4019
83	4052	4086	4120	4155	4190	4225	4262	4298	4335	4372
84	4410	4448	4487	4526	4566	4606	4648	4689	4731	4773
85	4816	4860	4905	4950	4995	5042	5088	5136	5184	5233
86	5283	5333	5384	5436	5489	5542	5597	5652	5708	5765
87	5822	5881	5941	6001	6063	6125	6189	6253	6319	6386
88	6453	6522	6593	6664	6737	6811	6886	6963	7041	7120
89	7201	7283	7367	7453	7540	7629	7719	7812	7906	8002
0·90	8100	8200	8302	8406	8513	8621	8732	8846	8962	9080
91	9201	9324	9452	9581	9714	9850	9989	1013	1028	1043
92	1058	1074	1090	1107	1123	1141	1158	1177	1196	1215
93	1236	1256	1277	1299	1321	1345	1369	1393	1419	1445
94	1473	1501	1530	1560	1592	1624	1658	1692	1728	1766
95	1805	1846	1888	1933	1979	2027	2077	2130	2185	2244
96	2304	2368	2436	2506	2582	2660	2744	2833	2928	3029
97	3136	3251	3374	3507	3649	3803	3970	4150	4347	4564
98	4802	5005	5358	5684	6052	6468	6945	7493	8134	8892
99	9801	1091	1230	1409	1647	1980	2480	3313	4980	9980

Further Exercises.—It will be found of much interest to study the effect of different substituents and of the position of substituents on the ionization constant.[1] For this purpose, determinations of the conductivity of the following acids may be made : acetic acid, glycollic acid, phenylacetic acid, phenylglycollic acid (mandelic acid) ; monochloracetic acid, dichloracetic acid, trichloracetic acid ; benzoic acid, *o*-, *m*-, and *p*-chlorbenzoic acids.

Strong Electrolytes.—In the case of strong electrolytes, it is found that the expression $\alpha^2/(1-\alpha)v$, where α is calculated from the ratio $\varLambda_c/\varLambda_0$, is not constant, but varies very markedly with the concentration. It had been found, however, by Kohlrausch that $\varLambda_c$ varies inversely as the square root of the concentration ; and an explanation of this has been found in the theory of interionic attraction put forward by Debye and Hückel. Accepting the theory of complete ionization, according to which the change of equivalent conductivity in dilute solution is due, not to a change in the number of the ions but to a variation of their mobilities owing to the action of interionic forces, Debye and Hückel calculated that the retardation of an ion is proportional to the square root of the concentration. By this reduction of ionic mobility, the value of $\varLambda_c$ varies inversely as the square root of the concentration. In the case of strong electrolytes, therefore, α is not a measure of the degree of ionization.[2]

EXPERIMENT.—*Determine the Equivalent Conductivity of Solutions of Potassium Chloride.*

In illustration of what has been said above, the equivalent conductivity of solutions of potassium chloride at 25°, in concentrations from N/50 to N/3200, should be determined, and the values plotted against the square root of the concentration. From the values so obtained and the value $\varLambda_0=150$ calculate, for each concentration, the value of $\alpha=\varLambda_c/\varLambda_0$, and the value of the expression $\alpha^2/(1-\alpha)v$.

Basicity of Acids.—It has been found that the difference between the equivalent conductivity of N/32 and N/1024 solutions of the sodium or potassium salt of an acid is approximately equal to $10.8 \times B$ units, where B represents the basicity of the acid. To determine the basicity of an acid, therefore, it is only necessary to determine the equiva-

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[1] See Wegscheider, *Monatsh.*, 1902, **23**, 289.

[2] It happens that in the case of uni-univalent electrolytes at concentrations not greater than 0·001 molal, the value of α is very nearly equal to the activity coefficient, γ.

lent conductivity of its sodium (or potassium) salt in a dilu-
tion of 32 litres and 1024 litres respectively, and to divide
the difference of the values so obtained by 10·8. The
nearest whole number then represents the basicity of the
acid.

EXPERIMENT.—*Determine the Basicity of Succinic Acid
or of Citric Acid.*

For the purpose of this experiment, sodium hydroxide
free from carbonate is required.[1]

This may be prepared as follows : [2] Sodium, cut into pieces about
half a centimetre thick, is dropped into an Erlenmeyer flask con-
taining CO_2-free water,[3] on the surface of which is a layer of ether.
The water dissolved in the ether reacts with the sodium, and the
sodium hydroxide passes into the water layer. The depth of the
ether must be at least three times the thickness of the pieces of sodium
used. At the end of the process, remove most of the ether by means
of a pipette and boil off the rest. The solution can be standardized
by means of succinic acid (the solution of which is also prepared with
CO_2-free water), using phenolphthalein as indicator.

In making up the $N/32$ solution of the salt, one may, if the
acid is solid, prepare exactly $N/32$ solution of caustic soda
and neutralize this with the solid acid, using a drop of
phenolphthalein as an indicator ; but in most cases it will
probably be found most convenient to have the acid also in
solution. In this case the caustic soda solution must be
stronger than $N/32$, and may suitably be about $N/16$.
Having ascertained the titre of the alkali solution, as much
of it is run from a burette into a measuring flask as contains
the amount of sodium hydroxide required to give an $N/32$
solution when diluted to a given volume, say 100 ml. This
is then neutralized carefully by means of the acid solution.
The acid must be added carefully, towards the end of the
process drop by drop, until the pink colour of the phenol-
phthalein, added as indicator, just entirely disappears ; better
a slight excess of acid than of alkali. The solution is now
made up to the given volume, say 100 ml., thus yielding an
$N/32$ solution of the sodium salt of the acid. The equivalent
conductivity of this solution is determined in the manner
previously described. The solution is then diluted by the

[1] For ordinary laboratory measurements, solutions prepared with
sodium hydroxide, "purified by alcohol," may be used.

[2] Cornog. *J. Amer. Chem. Soc.*, 1921, **43**, 2573.

[3] This is obtained by drawing a current of CO_2-free air through the
water. The air is freed from carbon dioxide by passage through a tube
containing soda-lime.

successive withdrawal of 10 ml. of the solution and addition of 10 ml. of water (p. 172), until the concentration is $N/1024$; and the equivalent conductivity at this dilution determined.

Additional Exercise.—From measurements of the conductivity of solutions of potassium permanganate and potassium persulphate, ascertain the basicity of permanganic acid and persulphuric acid.

Conductimetric Titrations.—Measurements of the electrical conductance can also be employed in order to determine the end-point of reactions between electrolytes, *e.g.* neutralization of acids and alkalies, precipitation reactions, etc. The method is of especial importance when one is dealing with coloured or turbid solutions, in which the change of colour of an indicator would be more or less masked, or with very dilute solutions.

Acid-alkali Titrations.—When a strong acid is added to an alkali, the conductance of the solution will decrease owing to the disappearance of hydroxide ion, and its replacement by the less mobile anion of the acid ; but when all the hydroxide ion has been removed, by combination with hydrogen ion from the acid added, then any further addition of acid will cause the conductance to increase, owing to the addition to the solution of free hydrogen ion. Since hydrogen ion has a much greater mobility than any other ion, the presence of a slight excess of free acid will cause a marked increase in the conductance. When, therefore, the conductance of the solution is plotted against the number of millilitres of acid added, a curve of the form shown in Fig. 78A, is obtained. The point of intersection of the two curves gives the number of millilitres of acid required to neutralize exactly the solution of the alkali.

When both acid and alkali are strong, one may carry out the titration from either side. The acid may be added to the alkali, or the alkali to the acid. In the latter case, there is first a diminution of the conductance owing to the replacement of hydrogen ion by a less mobile cation, and then, after the neutral point has been reached, an increase in the conductance, which is sharply defined owing to the fact that the OH' is also a highly mobile ion.

When, however, the acid is weak, it is necessary to add the acid to the alkali (*and in this case a strong alkali must be chosen*), and not the alkali to the acid. If the alkali is added to a weak acid, the minimum is not sharp owing to

the fact that the change in conductance is due not so much to the disappearance of the fast-moving hydrogen ion (which is present in comparatively small concentration, as to the replacement of the un-ionized acid molecules by the ions of the salt formed.   When, however, the acid is added to the alkali, the hydroxide ion is replaced by the much slower anion of the acid, and a consequent diminution of the conductance of the solution is produced.   As the acid is, however, only slightly ionized, and the ionization is further reduced by the presence of the neutral salt, the addition of excess of acid does not, in general, lead to an increase of the conduct-ance, but only to a sharp change in the direction of the conductance curves, as shown in Fig. 78, B.
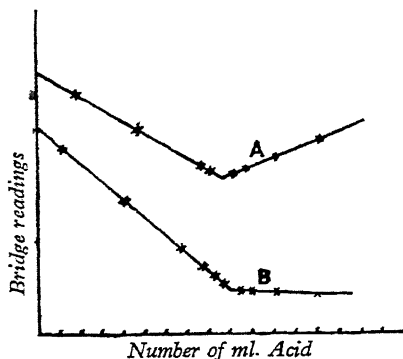
Number of ml. Acid

FIG. 78.

Strong acids, also, may be titrated in presence of weak acids,[1] and the basicity of an acid may be determined.[2]

Other Electrolytic Reactions. — The conductimetric method of titration may also be used to determine the end-point of various electrolytic reactions.[3]   Thus, in the case of the reactions,

$$NaCl + AgNO_3 = AgCl + NaNO_3$$
$$CH_3.COONa + HCl = CH_3.COOH + NaCl$$
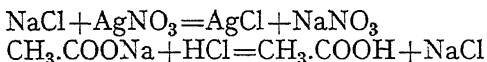
the conductance of the solution remains almost unchanged on addition of the silver nitrate or of the hydrochloric acid, because the conductance of sodium nitrate is similar to that of sodium chloride, and the conductance of sodium chloride is similar to that of sodium acetate.   When, however, excess of silver nitrate or of hydrochloric acid is added, the con-

[1] See Harned and Laird, *J. Amer. Chem. Soc.*, 1918, **40**, 1213 ; Eastman, *ibid.*, 1925, **47**, 332.

[2] See, for example, Rae, *J. Chem. Soc.*, **1931**, 876.

[3] Harned, *J. Amer. Chem. Soc.*, 1917, **39**, 252 ; Kolthoff, *Die Konduktometrischen Titrationen* ; Jander and Pfundt, *Leitfähigkeitstitrationen und Leitfähigkeitsmessungen* ; Britton, *Conductometric Analysis* ; Harms and Jahr, *Z. Elektrochem.*, 1935, **41**, 130.

ductance shows a sudden increase. In the case of the reaction, $MgSO_4+Ba(OH)_2=Mg(OH)_2+BaSO_4$, the resultants are both sparingly soluble and separate out from the solution. There is therefore a marked decrease of the conductance. On adding excess of barium hydroxide, the conductance rapidly increases.

Practical Methods.—In carrying out a conductimetric titration, a known volume of the solution to be titrated may be placed in a conductivity cell and the conductance determined as previously described (p. 169). The resistance which is inserted should be such that the bridge reading is about 50 cm. The titrating solution is then run in from a burette in small quantities at a time, and after each addition the solution is well mixed and the point of balance on the bridge wire is determined. The resistance in the box is kept the same throughout. A decrease in conductance is indicated by the point of balance moving towards the zero end of the wire. The bridge readings (which are proportional to the conductance) are plotted as ordinates against the number of millilitres of titrating solution added, and curves are drawn through the points obtained. The point of intersection of the curves gives the equivalence point.

To avoid the disturbing effects due to dilution, the concentration of the titrating solution should be five or ten times greater than the concentration of the solution to be titrated, the titrating solution being delivered from a microburette graduated to 0·01 ml.

The conductimetric method of titration can be greatly simplified and improved by rectifying the alternating current passing through the conductivity cell and measuring the fall of potential in the circuit by means of a millivoltmeter.[1] The rectification can be effected by means of a thermionic valve or, more simply and more satisfactorily, by means of a carborundum detector.[2] This possesses the advantage that it is unaffected by vibration. A diagram of the arrangement is shown in Fig. 79. Alternating current at about 3 volts is supplied by the transformer T, and is rectified by the crystal detector, X. The whole detector unit[3] is shown within the dotted frame in Fig. 79, and consists of

[1] The use in conductimetric titrations of an Evershed and Vignoles dionic water tester has also been recommended (Rae, *J. Chem. Soc.*, **1931**, 3143).
[2] Callan and Horrobin, *J. Soc. Chem. Ind.*, 1928, **47**, 337 T.
[3] Supplied by the Carborundum Co., Ltd., Manchester,

a small cell, potentiometer and condenser, as well as the crystal. In this arrangement a small positive bias is applied to the plate side of the detector, whereby the sensitivity is increased and the readings on the millivoltmeter rendered more steady. The fall of potential in the circuit through the variable resistance, R, can be measured on the milli-voltmeter, M. This measures, also, the current flowing and, with a fixed resistance at R, the conductivity of the solution in the cell C. During titration the solution is kept well stirred.

The electrodes of the conductivity cell consist of platinum wires (platinized), about half an inch in length and sealed into glass tubes containing mercury (Fig. 80), whereby con-
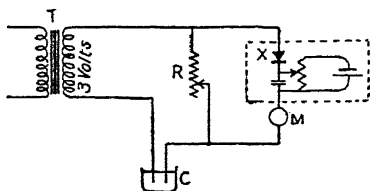
FIG. 79.
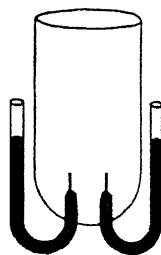
FIG. 80.

nection with the rest of the circuit can be made. The solution to be titrated having been placed in the cell, the resistance R is regulated so as to give a suitable initial reading on the millivoltmeter. The steadiness of the volt-meter readings is increased by using as high readings as possible. The bias applied to the detector must also be adjusted so as to give steady readings. The titrating solu-tion is then run into the cell from a burette, at first 0·2 ml. and later 0·1 ml. at a time, and after each addition the reading on the millivoltmeter is taken. As before, these readings (proportional to the conductance of the solution) are plotted against the amount of titrating solution added. Since these curves bend somewhat, the point of neutrality is obtained by drawing straight lines through the milli-voltmeter readings in the neighbourhood of the neutrality point, and finding the point of intersection.

EXPERIMENTS.—(I) 5 ml. of N/10–NaOH are placed in the conductivity cell and diluted to 50 ml. N-HCl is run in

from the micro-burette. $\cdot$(2) Titrate in the same way $N/10$-Na_2CO_3. (3) Titrate $N/10$-Na_2SO_4 (10 ml. diluted in cell to 40 ml.) with N-$BaCl_2$.

Solubility of Sparingly Soluble Salts.—Determinations of the conductivity may also be employed, very advantageously, for the determination of the solubility of sparingly soluble salts,[1] except salts of weak acids or weak bases.

If the concentration of the salt in the saturated solution is represented by c g.-equiv. per litre, the volume of solution containing 1 g.-equiv. will be $1/c$ litre or $1000/c$ ml. The equivalent conductivity of a solution is given by $\Lambda = 1000\ \kappa/c$, where κ is the specific conductance of the solution, and since the solution is very dilute, $1000\ \kappa/c$ may be taken as equal to the equivalent conductivity at infinite dilution, Λ_0.[2] If, therefore, the value of Λ_0 (or the sum of the ionic conductivities) is known, the concentration of the solute in the saturated solution may be calculated by means of the expression

$$c = \frac{1000\kappa}{\Lambda_0} \text{ g.-equiv. per litre.}$$

EXPERIMENT.—*Determine the Solubility of Lead Sulphate, or of Silver Chromate, in Water at* 20°.

The conductivity of the water employed should first be determined at 20°. A quantity of finely powdered lead sulphate or silver chromate is then shaken repeatedly with the conductivity water in order to remove any impurities of a comparatively soluble nature. The well-washed salt is then placed along with conductivity water in a hard-glass vessel, which is placed in a thermostat at 20°, and shaken from time to time. After intervals of about quarter of an hour, a quantity of the solution is transferred to a conductivity cell, and the conductivity determined.[3] This is repeated with fresh samples of the solution, until constant values are obtained.

The conductivity so determined is corrected by subtracting the conductivity of the water employed, and the solu-

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[1] See Böttger, *Z. physikal. Chem.*, 1903, **46**, 521 ; Kohlrausch, *ibid.*, 1908, **64**, 129 ; Prud'homme, *J. Chim. phys.*, 1911, **9**, 517 ; Johnson and Hulett, *J. Amer. Chem. Soc.*, 1933, **55**, 2258.

[2] Modern theory shows that this is not strictly correct. The value of Λ_0 must be decreased by a certain small amount which can be calculated by means of Onsager's equation.

[3] For the experiments in this section a conductivity cell with large electrodes placed a short distance apart should be used.

bility then calculated by means of the equation $c = \dfrac{1000 \cdot \kappa}{\Lambda_0}$.

This gives the number of gram-equivalents of salt in 1 litre of solution (or of water). To obtain the number of gram-molecules per litre, the solubility in gram-equivalents per litre must be divided by the valency of the metal. (For the solubilities of some sparingly soluble salts, see Appendix.)

The solubility of other sparingly soluble salts can be obtained in a similar manner. The value of Λ_0 can be obtained from the sum of the ionic conductivities (see Appendix).

Hydrolysis of Salts.—When the salt of a weak acid or base is dissolved in water, hydrolysis occurs, so that the conductance of the solution is now due partly to the ions of the salt and partly to the ions (more especially the hydrogen ion and hydroxide ion) of the acid or base formed by hydrolysis. If, however, a quantity of the weak acid or base which, in the presence of its salt, can be regarded as completely un-ionized, is added to the solution, the hydrolysis of the salt will be diminished, but the ionization will be unaffected. From measurements of the conductivity of pure solutions of the salt (in which, therefore, hydrolysis occurs), and of solutions containing excess of the weak base or acid, the degree of hydrolysis can readily be calculated.[1]

Considering here only the simplest case of a binary salt, say of a strong monobasic acid with a weak monoacid base, the hydrolytic equilibrium is given by the expression

$$\frac{K_b}{K_w} = \frac{(1-x)v}{x^2}$$

where v is the volume in litres containing 1 gram-molecule of salt ; x the degree of hydrolysis ; K_b the affinity constant of the weak base ; and K_w the ionic product of water. The amount of the unhydrolysed salt is represented by $(1-x)$, and of the free acid by x. The equivalent conductivity, Λ_v, of the solution of hydrolysed salt, therefore, is given by

$$\Lambda_v = (1-x)\Lambda_v' + x \cdot \Lambda_v'',$$

where Λ_v' and Λ_v'' are the equivalent conductivities at the dilution v litres of the unhydrolysed salt and of the strong acid respectively. The former, as has been pointed out, can

[1] Bredig, *Z. physikal. Chem.*, 1894, **13**, 321 ; Noyes, Kato and Sosman, *J. Amer. Chem. Soc.*, 1910, **32**, 159.

be determined by measuring the equivalent conductivity of the salt in presence of excess of the weak base. The degree of hydrolysis of the salt at the given dilution is then given by the expression

$$x = \frac{\varLambda_v - \varLambda_n'}{\varLambda_v'' - \varLambda_v'}$$

EXPERIMENT.—*Determine the Degree of Hydrolysis of Aniline Hydrochloride in Aqueous Solution at 25°.*

Make a solution (say N/32) of aniline hydrochloride in water. Place 20 ml. of this solution in a conductivity cell and determine the conductivity at 25°. Dilute the solution with water to N/64 and N/128, as described on p. 172, and determine the conductivity at each dilution. Make now a solution of aniline hydrochloride, not in pure water, but in an N/32-solution of aniline, and determine the conductivity at the same dilutions as before, the dilution of the original solution being carried out with the N/32-solution of aniline. From the conductivities so determined, calculate the degree of hydrolysis of aniline hydrochloride at each of the dilutions, the equivalent conductivities of hydrochloric acid at $v=32$, 64 and 128, being taken as 393, 399 and 401 respectively.

Calculation.—From the value of the degree of hydrolysis found calculate (1) the affinity constant of aniline, assuming the ionic product of water at 25° to be $1 \cdot 02 \times 10^{-14}$; (2) the ionic product of water, assuming the affinity constant of aniline to be $5 \cdot 3 \times 10^{-10}$.

CHAPTER XI

TRANSPORT NUMBERS

WHEN a current of electricity is passed through an electrolyte, it is found that the change of concentration at the two electrodes is, in general, not the same. It follows, therefore, that since equivalent amounts of positive and negative ions are discharged at the two electrodes, the velocity with which the ions move under the fall of potential must be different. From this difference in the velocity of migration of the two ions it follows that since the electricity is carried through the solution by the ions, the amount of electricity carried in one direction by the positive ions, must be different from that carried in the opposite direction by the negative ions; these two amounts being, indeed, in the ratio of the velocities of migration of the cation and anion respectively.

Since the total amount of electricity passed through a solution is proportional to the sum of the velocities, $u_c + u_a$, of the cation and anion, it follows that the fraction of the total current carried by the cation is $u_c/(u_c + u_a)$, and that carried by the anion $u_a/(u_c + u_a)$. These fractions are known as the *transport number* of the cation and anion respectively (Hittorf). The transport number can therefore be obtained by determining the total amount of electricity which passes through the solution, and the amount of one of the ions which has passed away from the space round one of the electrodes.

In this method of determining the transport number of an ion, it is assumed that change in the concentration takes place only in the neighbourhood of the electrodes, and that the intermediate portion of the solution remains unaltered. It is evident, therefore, that the current must not be allowed to pass for too long a time. Another reason, also, for limiting the time during which the current passes is that alteration in the composition would otherwise be caused by ordinary diffusion.

EXPERIMENT.—*Determine the Transport Numbers of the Silver Ion and Nitrate Ion in a Solution of Silver Nitrate.*

For this experiment the apparatus shown in Fig. 81 may be employed.[1]   The tubes A, B, and C are first filled with a solution of silver nitrate (about $N/20$), the composition of which *by weight* is determined by titration.   Into the tubes A and B there are fixed, by means of corks, two silver electrodes, made by fixing pieces of thick silver rod to copper
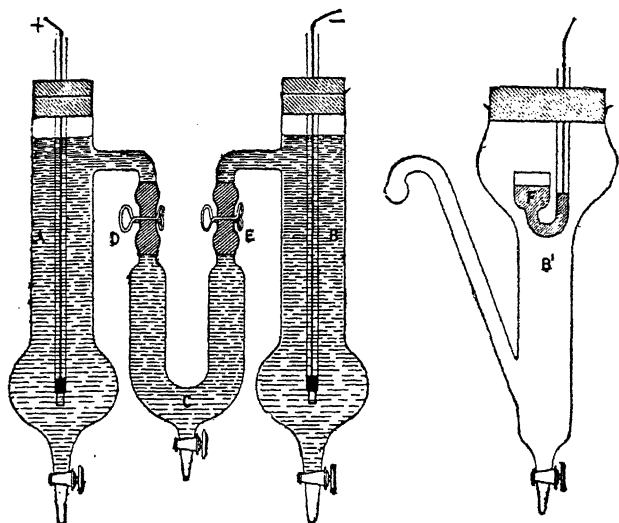
FIG. 81.

wires and cementing the latter into glass tubes so that only the silver is exposed.

The apparatus is now connected with a battery, and a current of about 0·01 or 0·02 amp. sent through the solution.[2] A milliammeter and a copper coulometer, together with a sliding resistance, should also be inserted in the circuit, all in series ; the ammeter being used for the approximate regulation of the current, and the coulometer for the deter-

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[1] Findlay, *Chem. News*, 1909, **100**, 185.   For other forms of apparatus, see Washburn (*J. Amer. Chem. Soc.*, 1909, **31**, 330) ; Noyes (*ibid.*, 1901, **23**, 37) ; Noyes and Sammet (*ibid.*, 1902, **24**, 944).

[2] Sufficiently accurate results can also be obtained with a current of about 7 milliamperes ; but too strong a current should not be used on account of the heating effect, and the consequent danger of convection currents causing a mixing of the different layers of solution.

mination of the total amount of electricity passed through the solution. The electrical potential which must be employed in order to give a current of about 10 milliamperes will depend, of course, on the resistance, and, therefore, on the dimensions of the apparatus employed. In general, a potential of 30–40 volts will be necessary.

As copper coulometer one may employ a beaker containing a copper solution of the composition given below, in which dip two electrodes, about 1·5–2 sq. cm., cut from copper sheet, the size being chosen so that the current density is about 0·01 amp. per sq. cm. The plate to be used as cathode must first be cleaned and weighed ; and at the conclusion of the experiment it is withdrawn from the solution, washed well with distilled water and with alcohol, dried in the hot air over a flame, and again weighed. While the experiment is in progress, a current of carbon dioxide, washed by bubbling through water, should be passed through the solution, in order to keep it stirred.[1]

The copper solution should have the following composition :—

Copper sulphate	.	.	150 g.
Sulphuric acid	.	.	50 g.
Alcohol	.	.	50 g.
Water	.	.	1000 g.

The same solution can be used repeatedly.

At the conclusion of the experiment,[2] the rubber tubes are closed by means of the clips D and E, and the anode liquid run off, through the tap at the bottom of the tube A, into a weighed flask. This tube and the electrode are then washed out with a little of the *original solution*, which is also allowed to run into the weighed flask. The solution is weighed and its composition determined by titration. The clip at D is then opened, and the intermediate solution contained in the tube C is run into a separate flask and analysed. The composition of this solution should be unchanged.

(It is sometimes convenient also to analyse the cathode solution. This can be run off in exactly the same manner as the anode solution.)

[1] See Richards, Collins, and Heimrod, *Z. physikal. Chem.*, 1900, **32**, 321.
[2] The current should be passed until about 0·05–0·1 gram of copper is deposited in the coulometer.

If the solution in the tube C does not have the same composition as the original solution, it shows that the experiment has been allowed to continue too long ; and it must therefore be repeated, the current this time being stopped after a shorter period.

The method of calculation will be made clear by the following example :—
Composition of silver solution before electrolysis—

> 9·973 g. of water
> 0·0847 g. ,, silver nitrate
>
> 10·058 g. ,, solution

That is, for every 9·973 g. of water there is 0·0847 g. of silver nitrate or 0·000498 g.-equivalent of silver.
After electrolysis, the solution had the composition—

> 26·76 g. of water
> 0·2818 g. ,, silver nitrate
>
> 27·04 g. ,, solution.

That is, for every 26·76 g. of water there is 0·2818 g. of silver nitrate, or 0·001658 g.-equivalent of silver.

If the solution had remained unchanged in composition, 26·76 g. of water would have been associated with $\dfrac{0·000498 \times 26·76}{9·973} = 0·001337$ g.-equivalent of silver.

There has been an increase, therefore, of 0·001658 − 0·001337 = 0·000321 g.-equivalent of silver.

The weight of copper deposited in the coulometer amounted to 0·0194 g. or to 0·000610 g.-equivalent ; and the total amount of electricity is proportional to this number.

If none of the silver had wandered away from the anode, there ought, therefore, to have been an increase of 0·000610 g.-equivalent. But the increase found amounted to 0·000321 g.-equivalent. Hence there must have wandered away, 0·000610 − 0·000321 = 0·000289 g.-equivalent of silver ; and this number must be proportional to the velocity of the silver ion. Hence the fraction of the total current carried by the cation amounts to $\dfrac{0·000289}{0·000610} = 0·474$.

From this it follows that the fraction carried by the anion amounts to 1 − 0·474 = 0·526. These two numbers, 0·526 and 0·474, are called the transport numbers of the anion and cation respectively.

EXPERIMENT.—*Determine the Transport Number of the Sodium Ion and Chloride Ion in a solution of Sodium Chloride.*

In the case of salts of metals which decompose water, it is evident that these metals cannot be used as electrodes. In their place one employs as anode a metal which passes into solution when the current is flowing (a soluble anode); and as cathode, mercury or platinum is used according to circumstances.

Prepare, by weighing, a solution of pure sodium chloride, containing about 1 per cent. of the salt. Fill the apparatus shown in Fig. 81 with this solution, the tube B being, however, replaced by B'. As anode use a rod of amalgamated zinc or cadmium fixed into a glass tube with sealing-wax; and as cathode use mercury, contained in a trumpet-shaped tube, F. Before the tube F is inserted in the tube B', place a concentrated solution of zinc chloride, of oily consistency, on the surface of the mercury, so as to form a layer about 1 cm. in depth. On the top of this, place carefully, to avoid mixing, a quantity of the solution of sodium chloride so as to fill completely the tube F. The purpose of the zinc chloride solution is to prevent the evolution of hydrogen and the production of OH'. Pass the electric current through the solution, as in the previous experiment, using a copper coulometer in circuit. At the conclusion of the experiment close the clips D and E and withdraw the anode and intermediate solutions for analysis, as explained above. The anode solution, after being weighed, may be made up to a definite volume, and its concentration ascertained by a volumetric determination of the chloride. The composition of the intermediate solution should be found unchanged.

In calculating the change in composition of the anode solution, it must be remembered that an amount of zinc (or cadmium) equivalent to the copper deposited in the coulometer has passed into solution. The solution, therefore, contains zinc (or cadmium) chloride and sodium chloride. To obtain the weight of water contained in a given weight of the solution, the amounts of these salts must be calculated and subtracted from the weight of the solution. The calculation of the transport number is then carried out in a manner analogous to that employed in the case of silver nitrate.

The transport number for Cl' in a solution of sodium chloride of the above concentration, at the mean temperature, is 0·61.

Moving-boundary Method.—Transport numbers may also be determined by measuring the rate of movement of a boundary between two solutions. For recent forms of suitable apparatus, the reader is referred to MacInnes and Brighton (*J. Amer. Chem. Soc.*, 1925, **47**, 994), Cady and Longsworth (*ibid.*, 1929, **51**, 1656), and Longsworth (*ibid.*, 1932, **54**, 2741).

Additional Exercises.—The hydration of ions may be studied from the changes of concentration of a non-electrolyte (*e.g.* carbamide) at the electrodes during electrolysis. (See Taylor and Sawyer, *J. Chem. Soc.*, 1929, 2095.)

CHAPTER XII

MEASUREMENTS OF ELECTROMOTIVE FORCE

JUST as, in hydrodynamics, the energy of falling water is determined not only by the amount of water that falls, but also by the height of fall, so also in electricity, the electrical energy involves the two factors, *amount of electricity*, and *fall of potential* or *electromotive force*. This latter factor constitutes the driving force, and its measurement is of the utmost importance.

For our present purpose, which is chiefly to study the relations between chemical and electrical energy, measurements of the electromotive force are of especial importance. When a chemical reaction takes place, it is said to be due to the action of chemical affinity, which cannot, however, in general be measured quantitatively, nor, indeed, qualitatively, except in a somewhat indefinite way by means of the heat of reaction. In the case, however, of electrolytic reactions which give rise to electrical energy, as, for example, in galvanic cells, the measure of the affinity is given by the electromotive force of the cell. Therefore, although the amount of electricity delivered by two cells may be the same, the energy need not be so ; for just as the chemical affinity in different reactions is different, so also is the electromotive force produced when these reactions take place in a galvanic cell so as to give rise to an electric current. Nor can the heat of reaction be taken as the measure of the electrical energy which a given cell will yield, because only in a few cases is the latter equal to the heat of reaction ; in most cases it is either greater or less. The electromotive force of a cell, therefore, is a measure not of the heat of reaction, but of the diminution of the free energy of a system, which is the thermodynamic expression of what was called above chemical affinity.

For this reason, and also on account of the problems which measurements of the electromotive force make it possible to

solve, such measurements form one of the most important sections of physical chemical practice.

Measurement of the E.M.F. of a Cell—Outline of the Method.—The method usually employed for the determination of the e.m.f. of a cell is essentially that known as the Poggendorff compensation method.

If a source of electricity, A (Fig. 82), of constant e.m.f. is connected with the two ends of a wire, CD, of uniform resistance, then the fall of potential along the wire will be uniform. The difference of potential between C and any point E of the wire will be proportional to the distance CE, and will be equal to the fraction CE/CD of the total fall of potential along the wire. If another cell, B, the e.m.f. of which is less than that of A, is inserted along with a suitable indicating instrument, such as a galvanometer, in a side circuit, CGBE, so that it is opposed to A, and if the sliding contact E is moved along the wire until no current passes through the measuring instrument, then the e.m.f. of B is equal to that of A multiplied by CE/CD.
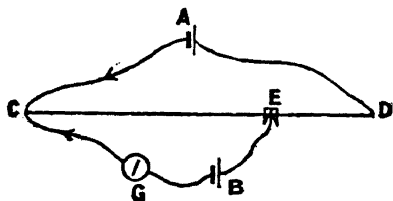
If the e.m.f. of the cell A, the working cell,

FIG. 82.

were quite constant and sufficiently accurately known, the measurement of an unknown e.m.f. could be made in the manner described. As a rule, however, neither of the above conditions is fulfilled. It is therefore necessary to have a standard cell, the e.m.f. of which is accurately known. The point of balance E on the bridge wire is first determined when the standard cell occupies the place of B ; and then the point E' (say) when the cell of unknown e.m.f. is in place of B. The unknown e.m.f. is then obtained from the relationship—

$$\frac{CE}{CE'} = \frac{\text{e.m.f. of standard cell}}{\text{unknown e.m.f.}}$$

The experimental arrangement just described has been called the Latimer-Clark potentiometer.

Apparatus.—*The Working Cell.*—As working cell A one must employ a cell with a greater e.m.f. than is to be measured. Since in all cases to be studied here, the e.m.f.

is less than 2 volts, the most convenient working cell to use is a lead accumulator, which, when fully charged, has an e.m.f. of somewhat over 2 volts. In order that the cell shall not run down too rapidly, and the e.m.f. therefore, fall, an accumulator of fairly large capacity should be employed. Where large fixed cells are not available, a portable accumulator of 30 to 40 ampere-hours capacity is very suitable.

Measuring Wire.—The measuring wire described on p. 158 may be employed, and may be calibrated as described on p. 162 before being used.

If the fall of potential along the bridge wire is 2 volts, then 1 mm. of wire corresponds to 2 millivolts. So far as
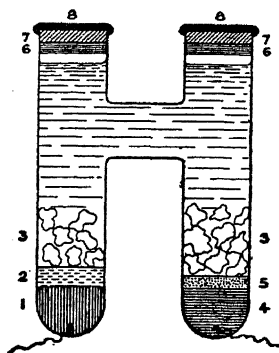
FIG. 83.

1. Mercury.
2. Paste of cadmium sulphate and mercurous sulphate.
3. Saturated solution and large crystals of cadmium sulphate.
4. Cadmium amalgam.
5. Small crystals of cadmium sulphate.
6. Paraffin.
7. Cork.
8. Sealing-wax.

the reading on the bridge wire is concerned, therefore, an accuracy of less than 1 millivolt can readily be attained, and this accuracy will be sufficient in the case of most of the experiments to be considered later.

Standard Cell.—Various cells have from time to time been recommended as standards of e.m.f., but the most convenient·and the one now most generally employed is the Weston standard cell (Fig. 83). This possesses the advantages not only of being easily reproduced, but also of having a small temperature coefficient of e.m.f. In this

cell, mercury forms the positive pole and a cadmium amalgam, containing 12·5 per cent. of cadmium, the negative pole. The electrolyte is a saturated solution of hydrated cadmium sulphate, $3CdSO_4,8H_2O$. The e.m.f. of the Weston standard cell has the following values :

Temperature.	e.m.f. in volts.
12°	1·0186
15°	1·0185
20°	1·0183
25°	1·0181

Purification of Mercury.—For use in the standard cell, as well as for many other purposes in physical chemistry, pure mercury, free especially from less noble metals such as zinc and lead, is required. When considerable amounts of mercury have to be treated, purification can be effected by drawing air, by means of a filter pump, through the mercury, the mercury being covered with a layer of sulphuric acid.[1] A more effective apparatus [2] is represented in Fig. 84.

FIG. 84.

The mercury to be purified is placed in the tall bottle, A, and in the body of the apparatus, B, there is placed a solution of mercurous nitrate acidified with nitric acid. The cork in the mouth of A fits loosely round the glass tube, C, and a notch is cut in its side so as to allow of the passage of air. The lower end of the tube C dips just below the surface of the mercury. Tube D is attached to a filter pump. When the pump is working, a series of small globules of mercury, separated by air, is drawn up the tube C and discharged into the liquid in tube B. The mercury can thus be kept circulating automatically through the solution of mercurous nitrate and acid until purification is complete. The mercury can then be run off from the bottom of the bottle, washed, if necessary, with distilled water and dried.

Where only small quantities of mercury have to be treated, the mercury may be shaken in a bottle with an acidified solution of mercurous nitrate [3] and then poured in a fine stream, by means of a funnel with drawn-out points, through a layer of mercurous nitrate acidified with nitric acid, contained in a tube to the lower end of
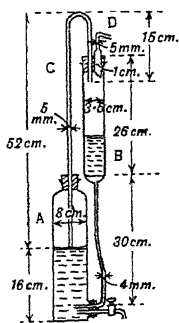
[1] For an automatically-acting arrangement, see Dixon and McKee, *J. Chem. Soc.*, 1923, **123**, 895.

[2] Jones, *J. Soc. Chem. Ind.*, 1930, **49**, 437T.

[3] Russell and Evans (*J. Chem. Soc.*, 1925, **127**, 2221) recommend the use of a concentrated solution of permanganate in 6N-sulphuric acid, to which also ferric sulphate is added.

which a bent capillary tube (1 mm. bore) is sealed (Fig. 85). The length of the capillary should be such that mercury ceases to flow from it when there is still a layer of mercury in the wide tube of about 2 cm. in depth. In filling this tube for the first time, pure dry mercury must first be poured into the tube, and then the solution of mercurous nitrate. By means of this apparatus, the mercury is obtained dry.

Null-point Detector.—For the purpose of determining the point of balance on the bridge wire (p. 195) a capillary electrometer [1] was, formerly, very generally employed. It has the advantage that, owing to its high resistance, it takes little current from the experimental cell and it is insensitive to electrical and magnetic disturbances. It has the disadvantage, however, that its accuracy is not very high and that it is liable to behave erratically in damp weather. Trouble, also, may be caused owing to the capillary mercury surface becoming dirty through formation of mercurous sulphate. In recent years, therefore, the capillary electrometer has been rapidly giving way to high resistance *galvanometers*.
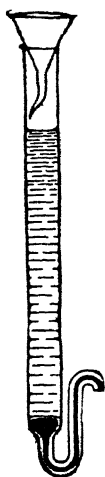
The most suitable galvanometers are of the moving-coil type, in which the current to be measured flows through a coil of fine wire suspended between the poles of a fixed magnet. For the most accurate measurements, the movement of the coil is read by means of a beam of light reflected from a small mirror attached to the moving system (mirror galvanometer). The light reflected from the mirror is caught on a scale placed at a suitable distance, about 1 metre, from the mirror. More generally, however, and in most cases more conveniently, a uni-pivot galvanometer is used and the movement of the coil is read by means of a pointer moving over a scale (pointer galvanometer). A number of such instruments, suited to different needs, are now on the market.

FIG. 85.

The *current sensitivity* of a galvanometer is the current required to give 1° of deflection or a movement of 1 mm. of a beam of light on a scale at 1 metre distance. The resistance of the galvanometer must be chosen according to the resistance in the external circuit.

[1] A description of this instrument was given in previous editions of this book.

Determination of the Electromotive Force of a Cell.—The apparatus is fitted up as shown in the diagram (Fig. 86). A is the working cell which is connected through the switch S_1 with the ends of the bridge wire ab. S_2 is a two-way switch by means of which either cell W_1 (standard cell) or W_2 (experimental or test cell) can be put in circuit. T is a tapping key, G is a galvanometer [1] and c the sliding contact on the bridge wire. The different connections are best made with flexible well-insulated wire.

The apparatus having been connected together, the current is allowed to flow from the working cell through the bridge wire. By means of the two-way switch, S_2, place the standard cell (W_1) in the circuit, and move the sliding contact c to, say, the 60 cm. mark on the measuring bridge. Momentarily depress the tapping key, T, and notice if there is any movement of the galvanometer pointer. If there is, move the contact c in one direction or the other until, on closing the tapping key, no deflection of the galvanometer pointer is observed. The position of the sliding contact is then read off on the millimetre scale.
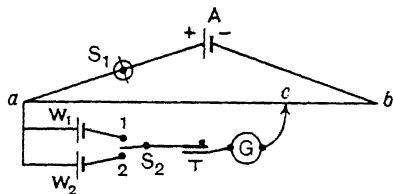
FIG. 86.

Having thus obtained the point of balance for the standard cell, switch S_2 is altered so as to put the test-cell, W_2, of unknown e.m.f., in the galvanometer circuit, and the sliding contact is moved until the point of balance is found. The point of balance for W_1 is again determined in order to make sure that the fall of potential along the wire has not altered.

If R_1 and R_2 are the readings for the standard cell W_1 and for the cell W_2 respectively, then—

$$\frac{\text{e.m.f. of } W_2}{\text{e.m.f. of } W_1} = \frac{R_2}{R_1},$$

or

$$\text{e.m.f. of } W_2 = \frac{R_2}{R_1} \times \text{e.m.f. of } W_1.$$

More Accurate Measurement.—With the simple metre bridge previously described, an accuracy of only about 1 millivolt can be attained. For more accurate work, the extended potentiometer

[1] It is advisable that the galvanometer zero should not be at the end of the scale, but in the middle, or at some intermediate point.

arrangement, represented diagrammatically in Fig. 87, may be used. A uniform wire, AB, 110 cm. in length, is stretched over a graduated millimetre scale, and connected, at the end A, with a series of, say, 15 resistance coils. These resistances are made accurately equal to one another and to 100 cm. of the wire AB. The total resistance from plug 15 to the end B of the wire will, therefore, be equivalent to the resistance of 1610 cm. of the wire; and if the e.m.f. applied to the ends, D and B, of the potentiometer resistance is made equal to 1·610 volts, the fall of potential in each of the resistance coils and along 100 cm. of the wire AB will be equal to 0·1 volt. Each centimetre of the wire will represent a fall of potential of 1 millivolt, and each millimetre a fall of potential of 0·1 millivolt.

In using this potentiometer one proceeds as follows :—The positive pole, say, of the working cell, C, is connected with the plug 15, and the negative pole with the end B of the resistance wire.
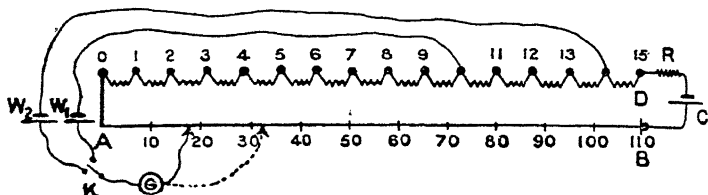
FIG. 87.

The positive pole of a standard cadmium cell, W_1 (e.m.f. $=1·0185$ volts), is connected with the plug 10 and the sliding contact is placed at the point 18·5 cm. on the wire. The resistance R in the working-cell circuit is then adjusted so that no current is shown by the galvanometer on closing the key K. The total fall of potential in the potentiometer will now be 1·610 volts, and the e.m.f. of a cell can be read off directly from the resistance plug and the straight wire. Thus, if balance is obtained when the positive pole of cell W_2 is connected with plug 14 and the sliding contact is at 32·5 cm., the e.m.f. of W_2 will be 1·4325 volts. To make sure that no change of e.m.f. takes place in the working cell during the measurements, the reading with the standard cell should be checked before and after making the reading for the unknown cell.

Instead of the resistance coils of the potentiometer being arranged in a line, as shown in Fig. 87, it is now customary to arrange them in a ring, and the wire AB is wound on a drum which can be rotated against a sliding contact. The resistances are all arranged in a box, and in this way the apparatus is rendered more compact.[1]

With the potentiometer just described, a high-resistance mirror galvanometer should be employed. In order to protect the galvanometer from too strong currents while the point of balance is being found, a resistance of 5000–10,000 ohms should be placed in the galvanometer circuit. On approaching the point of balance, this resistance should be cut out.

[1] Such an apparatus is made, for example, by the Cambridge Instrument Co., Ltd., and by Leeds and Northrup Co.

Potentiometer - Voltmeter Method.—Modifications of the Latimer-Clark potentiometer have been introduced for the measurement of the e.m.f. of a cell, and these modifications are specially useful when varying values of the e.m.f. have to be determined, as in potentiometric titrations (p. 234). One such modification is represented diagrammatically in Fig. 88. The working cell, A, is connected with the ends of a resistance ab, such as a double rheostat which allows of coarse and fine adjustment, and the test-cell, B, is connected with one end of the resistance and with the sliding contact c through the galvanometer, G. If the positive pole of the cell A is connected with the end a of the resistance, the positive pole of the cell B must also be connected with a. Across the resistance ac a millivoltmeter is inserted. In making a measurement of the e.m.f. of B, the sliding contact c is moved until, on closing the tapping key[1] T, no current is indicated by the instrument G. The e.m.f. of the cell is then read off on the millivoltmeter V. It should be noted that the voltmeter must be left constantly in the circuit while the resistance is being adjusted to the point of balance.
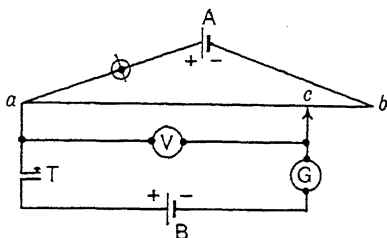
FIG. 88.

Use of the Triode Valve.—In recent years the electron tube or thermionic valve has come into widespread use in measurements of electromotive force, and its use has the great advantage that practically no current is drawn from the cell during measurement.

When the filament of the valve is raised to incandescence by an electric current, the electrons which are emitted are attracted by the positively charged plate (anode) and repelled by the negatively charged grid. The current which is set up in the plate circuit may be considered as made up of the (constant) current depending on the valve and the applied potentials, and of the (variable) current depending on the negative grid potential. This

---

[1] The tapping key should be kept closed for as short a time as possible so that the current drawn from the test-cell may not disturb the equilibrium between the electrodes and the solution.

latter current is a linear function of the potential applied to the grid.

A number of different arrangements have been introduced; the one to be described here is due to Morton,[1] and has proved very satisfactory. It is represented in Fig. 89. The plate of the valve is maintained at a positive potential by means of a 60-volt " high tension " dry battery, B_2. A constant current, adjusted by means of the resistance R_1 (30 ohms) is passed through the filament from the 2-volt accumulator cell, B_3. B_1 is a 1·5-volt dry cell, the negative pole of which is connected to the grid of the valve, and C is the cell under investigation.
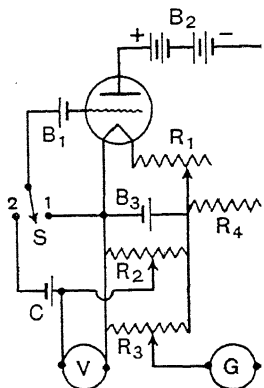
FIG. 89.

In carrying out a determination of the e.m.f. of the cell C, the filament is caused to glow by passage of current from B_3, and the switch S is placed in position 1. The normal anode current, which now flows through the galvanometer G, is balanced out by adjustment of the resistance R_3. Switch S is then placed in position 2 so that the cell C, the e.m.f. of which is to be determined, is included in the grid-filament circuit. The resistance R_2 is then adjusted so that the galvanometer is undeflected. The e.m.f. of the cell C is thus balanced by the fall of potential in the resistance R_2, and this is read off on the millivoltmeter V. The switch S should be placed in position 1 again to ensure that no change has taken place in battery voltages or valve characteristics.

A valve may also be used in conjunction with a precision potentiometer for the determination of the e.m.f. of a cell, as indicated by the arrangement shown in Fig. 90. S_1 is a three-position switch, with twelve contacts, and makes the following connections : Position 1 : 2–3, 8–9, 4–5, 10–11 ; Position 2 : 1–2, 7–8, 4–5, 10–11 ; Position 3 : 5–6, 11–12, 2–3, 8–9. The portion below the dotted line represents the potentiometer and its connections, and the two leads from the valve unit are joined to the galvanometer terminals of the potentiometer, the tapping key of which is short-circuited. R_4 is the potentiometer slide wire ; R_5 is the potentiometer main resistance ;

[1] *Pharm. J.*, 1927, **118**, 761 ; *T. Faraday Soc.*, 1928, **24**, 14. See also Garman and Droz, *Ind. Eng. Chem. (Anal.)*, 1939, **11**, 398.

R_6 is the standard cell compensating resistance; and R_7 is the potentiometer rheostat. S_2 is a double-pole, double-throw switch, St is the standard Weston cell and C is the cell whose e.m.f. is to be determined. The switch S_1 is placed in position 1 and S_2 is placed in " off " position, and the galvanometer deflection annulled by adjustment of R_2. S_1 is then placed in position 2 and S_2 is made to connect 2–3 and 5–6, and the current balanced out by adjustment of R_7. S_2 is then made to connect 1–2 and 4–5, and balance made by adjustment of R_4 and R_5.

The e.m.f. of the cell is then given directly by the readings of the potentiometer. With S_1 in position 3, the reading can be checked by the usual direct potentiometric method.

Seat of Electromotive Force of a Cell.—When a galvanic cell is inserted in a circuit, it is, in general, possible for differences of potential to occur at different points of the circuit. Thus, suppose the two poles of the cell—

| metal I | solution containing ions of metal I |

| solution containing ions of metal II | metal II |

to be connected together through a length of resistance wire. Then, sudden differences of potential are possible (1) at the junctions of the resistance wire with the poles; (2) at the junction between the metal I and the solution; (3) at the junction between metal II and the solution; (4) at the

FIG. 90.

junction between the two solutions. Under ordinary conditions, when the temperature is constant, the potential differences under (1) vanish. Not so, however, the potential differences between the two solutions (liquid junction or diffusion potential). Here an appreciable potential difference may exist, due, as the theory shows, to the difference in the velocities of migration of the ions. In some cases this potential difference can be calculated, but not in all cases;
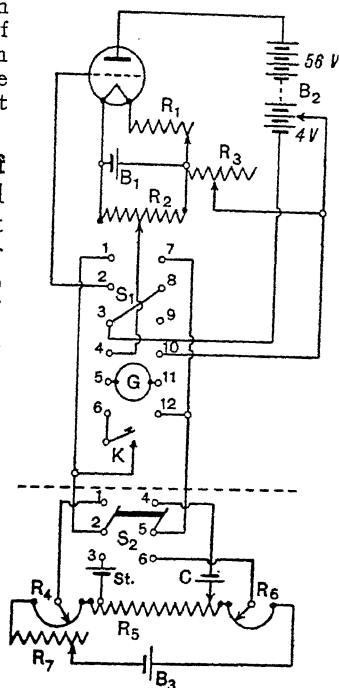
and it is better, where possible, to reduce this diffusion potential so as to make it negligible. Two chief ways of doing this are, first, to have present in the two solutions a relatively large (and equal) concentration of an indifferent electrolyte (potassium nitrate being frequently useful for this purpose) ; and, second, to insert between the two solutions a saturated solution of potassium chloride or of ammonium or potassium nitrate. When this is done, the chief and, practically, the only differences of potential occur at the junctions of the metals with the solutions ; and, therefore, the e.m.f. of the cell will be equal to the algebraic sum of these potentials.

The difference of potential between a metal electrode and a solution of one of its salts may be regarded as due to the passage into solution and ionization of the metal (in which case the electrode becomes negative to the solution), or to the discharge of the metal ions in the solution at the electrode (in which case the electrode becomes positive to the solution).

The potential which is observed will therefore depend on the metal which forms the electrode, and also on the concentration of its ions in the solution surrounding it (see below). When the metal is positive with respect to the solution, it is said to have a positive $(+)$ potential ; when it is negative to the solution, it is said to have a negative $(-)$ potential. This convention is, however, not universally employed.

Measurement of Single Electrode Potentials.—In order to measure the potential between an electrode and a solution, it is necessary to have another electrode and solution, the potential difference between which is known. As standard electrode one may employ what is generally known as the *normal calomel electrode.* This consists of mercury in contact with a normal solution of potassium chloride saturated with mercurous chloride.

Preparation of the Calomel Electrode.—As a vessel to contain the mercury and the solution, one may use a small, wide-mouthed bottle or a short glass cylinder with foot; but one of the most convenient forms of vessel is shown in Fig. 91.[1] It consists of a glass tube furnished with a bent side tube A, and a short straight side tube B, near the top. It is most convenient to have the tube A in two portions connected by rubber tubing, so that the free end can be detached and washed out when necessary. Over the end

[1] Various modifications of this electrode are in use.

of the side tube B there should be passed a piece of rubber tubing which can be closed by a spring or screw clip. Connection with the mercury electrode is effected by means of a platinum wire, either sealed into the bottom of the electrode vessel, or sealed into a glass tube and passed through a rubber stopper in the mouth of the tube. In the latter case, electrical connection is made by means of mercury in the tube C, into which an amalgamated copper wire dips ;
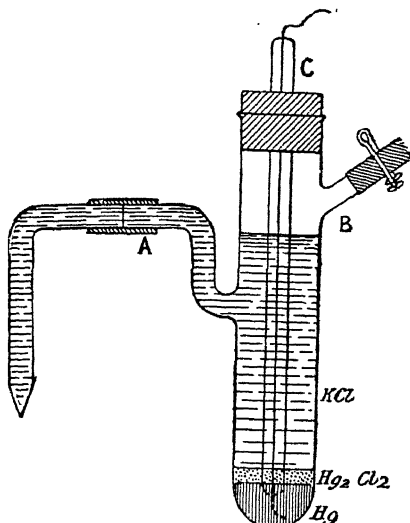

FIG. 91.

or the copper wire may be fused to the platinum wire before the latter is sealed into the tube.

First prepare the normal solution of potassium chloride, using pure recrystallized potassium chloride (dried) for the purpose. In the bottom of the electrode vessel, previously thoroughly dried or washed out with the solution of potassium chloride, place a small quantity (1–2 ml.) of pure mercury (p. 197), and over this a layer of calomel paste. This paste is prepared by rubbing together in a mortar calomel and mercury with some of the solution of potassium chloride. It is then washed two or three times with a quantity of the potassium chloride solution, the mixture being allowed each time to stand until the calomel has settled, and the solution then decanted off. Finally, the paste is shaken up with the remaining quantity of the potassium chloride solution (in order to saturate the latter with calomel), which should then be decanted off and kept in a stoppered bottle for future use.

Having placed the mercury and the calomel paste in the tube,

insert a rubber stopper or paraffined cork carrying the glass tube C with platinum wire, which must dip into the mercury at the bottom of the tube. The vessel is then filled with the solution of potassium chloride saturated with calomel and mercury, by sucking in the solution through the bent side tube A, and then closing the rubber tube on B with a clip.

Various other forms of the calomel electrode are on the market. In that shown in Fig. 92, there is a small reservoir, R, which holds a supply of potassium chloride solution from which the main vessel, K, can be replenished and by means of which a continuous liquid con-nection through the capillary system can be secured.

Owing to uncertainty in the determination of the absolute values of the potential, it is customary to determine only the relative poten-tial referred to the value of some standard electrode taken as zero. It is now usual to take as standard electrode, the hydrogen electrode with hydrogen at atmospheric pres-sure and with a solution containing hydrogen ion at *unit activity*, the potential of this electrode being taken as zero at all temperatures.
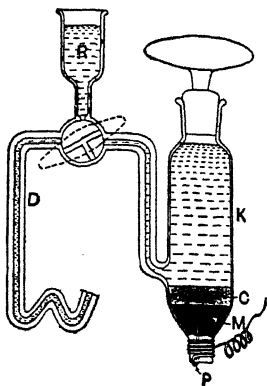
FIG. 92.

This electrode is known as the *normal hydrogen electrode* (p. 216).

In actual measurements of electrode potentials it is customary not to use the normal hydrogen electrode but the calomel electrode, and it is therefore necessary to know the potential of this electrode referred to the normal hydrogen electrode, for different concentrations of KCl. The following values have been obtained for temperatures between 15° and 40° :

0·1 N-KCl : $E = 0·3335 - 0·00007 \ (t - 25°)$
N-KCl : $E = 0·2812 - 0·00024 \ (t - 25°)$
Saturated KCl : $E = 0·2422 - 0·00076 \ (t - 25°)$

Unless otherwise stated, electrode potentials will always be given on the hydrogen standard.

Electrode Potentials.—When a metal is placed in a liquid, there is, in general, a potential difference established between the metal and the solution owing to the metal yielding ions

to the solution, or the solution yielding ions to the metal. In the former case, the metal will become negatively charged to the solution ; in the latter case, positively charged.

Since the total e.m.f. of a cell is (or can in many cases be made practically) equal to the algebraic sum of the potential differences at the two electrodes, it follows that if the e.m.f. of a given cell, and the value of the potential difference at one of the electrodes, are known, the potential difference at the other electrode can be calculated.   For this purpose, use is made of the standard calomel electrode, which is combined with the electrode and solution between which one wishes to determine the potential difference.

In the case of any particular combination, such as the following—

$$\text{Zn} \mid \text{N-ZnSO}_4 \mid \text{Hg}_2\text{Cl}_2 \text{ in N-KCl} \mid \text{Hg}$$
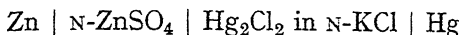
the positive pole of the cell can always be ascertained by the way in which the cell must be inserted in the side circuit (Fig. 86, p. 199), in order to obtain a point of balance on the bridge wire.   In order to obtain a point of balance, the cell must be opposed to the working cell ; and therefore, if the positive pole of the latter is connected with the end *a* of the bridge wire, it follows that the positive pole of the cell in the side circuit must also be connected with *a*.

The e.m.f. of the above cell at 18° is 1·082 volts, and from the way in which the cell has to be connected to the bridge wire, mercury is found to be the positive pole ; hence, the current must flow *in the cell* from zinc to mercury.   An arrow is therefore drawn under the diagram of the cell to show the direction of the current, and beside it is placed the value of the e.m.f., thus—

$$\text{Zn} \mid \text{N-ZnSO}_4 \mid \underset{\underset{\text{1·082}}{\longrightarrow}}{\text{Hg}_2\text{Cl}_2 \text{ in N-KCl}} \mid \text{Hg}$$
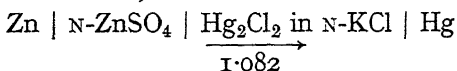
It is also known that the mercury is positive to the solution of calomel, so that the potential here tends to produce a current from the solution to the mercury.   This is represented by another arrow, alongside of which is placed the potential difference between the electrode and the solution, thus—

$$\text{Zn} \mid \text{N-ZnSO}_4 \mid \text{Hg}_2\text{Cl}_2 \text{ in } \underset{\underset{\text{0·281}}{\longrightarrow}}{\text{N-KCl} \mid \text{Hg}}$$
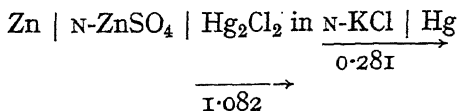
$$\underset{\text{1·082}}{\longrightarrow}$$

Since the total e.m.f. of the cell is 1·082 volts, and since the potential of the calomel electrode is 0·281 volt, it follows that the potential difference between the zinc and the solution of zinc sulphate must be 0·801 volt, referred to the normal hydrogen electrode, and this also must assist the potential difference at the mercury electrode. Thus we have—

$$\underset{\underset{\longrightarrow}{0\cdot801}}{Zn} \mid N\text{-}ZnSO_4 \mid Hg_2Cl_2 \text{ in } N\text{-}KCl \mid \underset{\underset{\longrightarrow}{0\cdot281}}{Hg}$$

$$\underset{\longrightarrow}{1\cdot082}$$
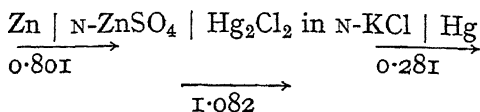
From the diagram it is seen that there is a tendency for positive electricity to pass from the zinc to the solution, *i.e.* the zinc gives positive ions to the solution, and must, therefore, itself become negatively charged relatively to the solution. The potential difference between zinc and the normal solution of zinc sulphate is therefore —0·801 volt. By adopting the above method, errors both in the sign and in the value of the potential difference can be readily avoided.

Preparation of Electrodes.—The copper and zinc electrodes to be used in the following experiment are prepared as follows : Pieces of pure zinc and copper rod, about 3 cm. in length, are soldered to fairly thin, insulated copper wire, and then cemented into glass tubes by means of sealing-wax, care being taken that the soldered junction is completely protected by the wax. Before use, the zinc electrodes are amalgamated by placing them in dilute sulphuric acid and rubbing mercury over them with a mop of cotton-wool ; after which they are well washed with distilled water. The copper electrodes, on the other hand, should first be cleansed by rubbing them with emery-paper or by dipping them in dilute nitric acid, and then, after being washed, coated electrolytically with copper. For this purpose, the solution of copper sulphate used in the coulometer, p. 190, may be employed, a strip of copper being used as anode. In order to obtain a fine, adherent deposit, a small current density (not exceeding 0·5 amp. per 100 sq. cm. at the cathode) should be used. At least two electrodes should be prepared in the above manner from each metal ; and before use, the uniformity of each set of electrodes must be tested by determining whether they give any e.m.f. when immersed in the same solution of copper sulphate (in the case of the

copper electrodes) or of zinc sulphate (in the case of the zinc electrodes).

Testing the Uniformity of the Electrodes.—Fix the electrodes into tubes like the one used for the standard electrode (p. 205, cf. Fig. 93), and fill the tubes with a solution of copper sulphate (in the case of the copper electrodes) and with a solution of zinc sulphate (in the case of the zinc electrodes). Decinormal solutions of the salts may be used for this purpose. Liquid connection between the electrodes is made by means of an intermediate solution of copper sulphate or of zinc sulphate (Fig. 93).

Fit up the apparatus as shown in Fig. 86, p. 199, replacing the cell W_2 by the cell Cu—solution of $CuSO_4$—Cu
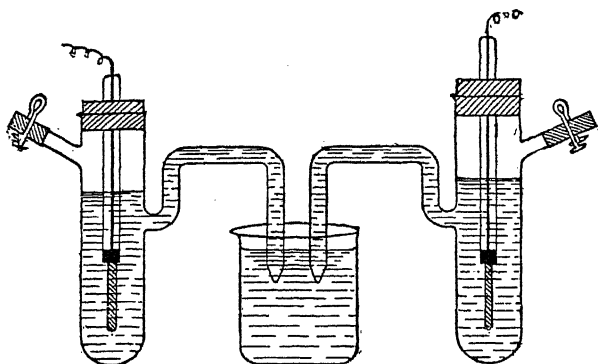
FIG. 93.

or the cell Zn | solution of $ZnSO_4$ | Zn connected in series with the standard cell W_1. By means of the two-way key, the point of balance on the bridge wire is determined, with the cell W_1 alone in the circuit, and then for the cell W_1 in series with one of the above cells. If the two copper (or zinc) electrodes are uniform, the point of balance should be the same in the two cases, *i.e.* the cells Cu | solution of $CuSO_4$ | Cu and Zn | solution of $ZnSO_4$ | Zn should exhibit no e.m.f. If, however, an e.m.f. of more than 1 millivolt should be found (for method of calculation, see p. 211), then the two copper (or zinc) electrodes should be placed in a solution of copper sulphate (or zinc sulphate) and short-circuited for several hours a day, until they no longer give an e.m.f. when placed in the same solution.

14

EXPERIMENT.—*Determine the Potential Difference between Zinc and a Solution of Zinc Sulphate, and between Copper and a Solution of Copper Sulphate.*

Having prepared uniform zinc and copper electrodes as described above, fix them into the electrode vessels as before, and fill the latter with deci-normal solutions of zinc sulphate and copper sulphate respectively. In order to determine the potential difference between the metal and the solution, each electrode is combined separately with a standard calomel electrode (p. 206) by means of an intermediate solution [1] of potassium chloride or ammonium nitrate (3-norm.) to form a galvanic cell in the manner shown in the diagram, Fig. 93.

The apparatus is fitted up as shown in Fig. 86, p. 199, W_2 now representing the cell

$$\text{Zn} \mid \text{o·1N-ZnSO}_4 \mid \text{KCl} \mid \text{Hg}_2\text{Cl}_2 \text{ in N-KCl} \mid \text{Hg}$$

or $$\text{Cu} \mid \text{o·1N-CuSO}_4 \mid \text{KCl} \mid \text{Hg}_2\text{Cl}_2 \text{ in N-KCl} \mid \text{Hg}$$
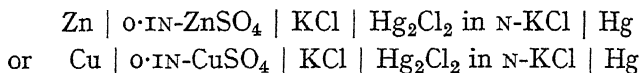
As it will, in general, be unknown which is the positive and which the negative electrode of the above combinations, one of the electrodes is connected with the end a of the bridge wire and the other is connected through the 2-way switch S_2 to the galvanometer. If no point of balance can be obtained, *i.e.* if the galvanometer pointer moves in one direction only, no matter where the sliding contact is placed, this shows that the wrong pole (the negative pole) has been connected to a. The connections are therefore altered so as to connect the positive pole of the cell to a. It should now be possible to obtain a point of balance on the bridge wire. One can in this way determine which is the positive and which the negative pole of the cell under investigation. If the e.m.f. of the cell W_2 is small, the point of balance will be near the end a of the bridge wire, and in this case the error in reading will be comparatively large. In such a case, it is better to connect the cell W_2 in series with the standard cell W_1. This can be done very simply by connecting the positive pole of W_2 with the point 1 of the 2-way switch. When, then, the 2-way switch is in position 1, only the standard cell W_1 will be in the galvanometer circuit; but when the switch is in the position 2, the two

---

[1] This intermediate solution, which is known as a " salt bridge," is inserted in order to diminish the liquid junction potential or diffusion potential at the junction of the liquids.

cells W_1 and W_2 will be connected in series, and the point of balance on the bridge wire will correspond to the sum of the e.m.f.'s of the standard cell and the cell W_2.

Several readings are taken, alternately, of the point of balance for the standard cell alone and for the standard cell plus the cell W_2. The e.m.f. of W_2 is then obtained from the equation (cf. p. 199)—

$$\frac{\text{e.m.f. of } W_1 + W_2}{\text{e.m.f. of } W_1} = \frac{R_2}{R_1}$$

where R_2 and R_1 are the readings for the standard cell plus W_2, and for the standard cell alone, respectively. Putting the value of the e.m.f. of the standard cell equal to 1·019 volts (p. 197), one finds—

$$\text{e.m.f. of } W_2 = \left(\frac{R_2}{R_1} \times 1·019\right) - 1·019 \text{ volts.}$$

From this, knowing the potential of the calomel electrode (p. 206), the potential between the copper and copper sulphate or zinc and zinc sulphate can be calculated (see p. 207).

Further Measurements.—Having determined in the above manner the electrode potentials, Zn | 0·1N-ZnSO₄ | and Cu | 0·1N-CuSO₄ determine, in the same way, the electrode potentials Zn | 0·01N-ZnSO₄ and Cu | 0·01N-CuSO₄. Further, determine t e e.m.f. of two or more of the combinations : Zn | 0·1N-ZnSO₄ | KCl | 0·1N-CuSO₄ | Cu ;   Zn | 0·01N-ZnSO₄ | KCl | 0·1N-CuSO₄ | Cu ;   Zn | 0·1N-ZnSO₄ | KCl | 0·01N-CuSO₄ | Cu ;   Zn | 0·01N-ZnSO₄ | KCl | 0·01N-CuSO₄ | Cu ; and compare the values of the e.m.f. found with the sum of the electrode potentials as determined above.

Influence of Concentration.—It has already been remarked that the potential difference between a metal and a solution of one of its salts depends on the concentration of the metal ions in the solution ; and this dependence will have already become evident from the experiments just described.

According to Nernst, the change in the electrode potential with concentration is given by the expression

$E = E_0 + 2·303 \dfrac{RT}{zF} \log_{10} \dfrac{C}{C_0}$, where E is the potential difference

for the *ionic* concentration C, and E_0 that for the concentration C_0. R is the gas constant and has the value 8·32 volt-coulombs ; T is the absolute temperature at which the

experiment is made ; z is the valency of the ion furnished by the electrode ; and F is 1 faraday (96,500 coulombs. E must be taken with its proper sign. From the above equation it follows that if the electrode potential is positive, it will diminish with dilution, and if it is negative, it will increase with dilution, *i.e.* it will become more negative.

Since it is with the effective concentration of the ion that one is concerned, that is, with the *ionic activity*, it is better to represent the relation between electrode potential and ionic activity by the expression $E = E_0 + 2 \cdot 303 \dfrac{RT}{zF} \log_{10} \dfrac{a}{a_0}$.

The numerical values of $2 \cdot 303 \dfrac{RT}{F}$ at 0°, 10°, 15°, 18°, and 25° C. are as follows :—

T	$2 \cdot 303 \dfrac{RT}{F}$
273°	0·0542
273+10°	0·0561
273+15°	0·0571
273+18°	0·0577
273+25°	0·0591

If the ratio of ionic activities is as 10 : 1, $\log_{10} a/a_0$ will be equal to unity. Consequently, if the metal ion is univalent, a tenfold increase or diminution in the activity of the metal ions will, at 15°, produce a change in the potential difference between the metal and the solution of 0·0571 volt. If the metal is z-valent, the corresponding change in the potential difference will be 0·0571/z volt.

EXPERIMENT.—*Determine the Influence of Concentration on the Potential Difference between Silver and Solutions of Silver Nitrate.*

Prepare two silver electrodes from stout silver wire, cementing them into tubes as in the case of zinc and copper electrodes (p. 208). The electrodes should be coated with a fresh deposit of silver, and the uniformity of the electrodes must be tested in the manner given for the zinc and copper electrodes (p. 209). The e.m.f. of the cells—

Ag | 0·1N-AgNO$_3$ | N-KNO$_3$ | Hg$_2$Cl$_2$ in N-KCl | Hg
and Ag | 0·01N-AgNO$_3$ | N-KNO$_3$ | Hg$_2$Cl$_2$ in N-KCl | Hg
should then be measured as described above.

On the assumption that the cation and anion have the same activity, the activity of the cation (silver ion) can be put equal to $\gamma \cdot c$, where γ is the activity coefficient of the electrolyte and c is the concentration. In the case of silver nitrate the activity coefficients in deci-normal and centi-normal solution respectively, are 0·72 and 0·90.

Concentration Cells.—Since the potential difference between a metal and its solution depends on the concentration of the latter, and since the e.m.f. of a cell depends on the differences of potential at its poles (electrodes), it follows that a combination of two electrodes of the same metal dipping in solutions of a salt of the metal of different concentrations will possess an e.m.f. and can give rise to a current. A cell of this description, the e.m.f. of which is due to a difference in the concentration of the same electrolyte around the two electrodes, is known as a *concentration cell*.[1]

In such cases the e.m.f. is not merely equal to the sum of the electrode potentials as measured against a calomel electrode, but involves also the potential difference at the junction of the two solutions, and for a uni-univalent electrolyte at 18°, is given by the expression—

$$E = \frac{2 \cdot u_a}{u_c + u_a} \cdot 0 \cdot 0577 \log_{10} \frac{a_1}{a_2},$$

In the above equation, $\dfrac{u_a}{u_c + u_a}$ represents the transport number of the anion, while a_1 and a_2 are the activities of the metal ions in the two solutions. By eliminating the diffusion potential between the two solutions (p. 204), one obtains $E = 0 \cdot 0577 \log_{10} \dfrac{a_1}{a_2}$. In the case of experiments carried out at a normal room temperature of 15°, the number 0·0571 should be used in place of 0·0577. When the metal ion is z-valent, the e.m.f. is given by the expression $E = \dfrac{0 \cdot 0577}{z} \log_{10} \dfrac{a_1}{a_2}$ at 18°.

EXPERIMENT.—*Determine the Concentration (Activity) of Silver Ions in a given Solution.*

In order to determine the concentration of silver ions in a given solution, it is only necessary to measure the e.m.f. of a cell of the typ_

Ag | solution containing Ag· of activity a_2 | solution containing Ag· of activity a_1 | Ag
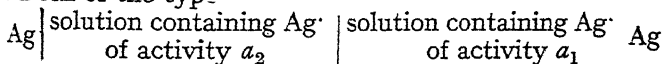
[1] Strictly, a " concentration cell with migration."

For the purpose of this experiment, a 0·01N-solution of silver nitrate may be taken as the solution in which the activity of silver ions is to be determined. Prepare, therefore, the following cell—

$$\text{Ag} \mid \text{0·01N-AgNO}_3 \mid \text{0·1N-AgNO}_3 \mid \text{0·1N-AgNO}_3 \mid \text{Ag}$$
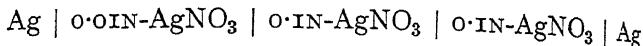
after the pattern of the cell shown in Fig. 93, p. 209. The silver electrodes should be prepared as described on p. 212, their uniformity being ascertained before they are employed for the measurements. The e.m.f. is then determined at room temperature (say, 15°), as in the experiment, p. 210. Putting the transport number of the anion equal to 0·528, the activity of the silver ions in the 0·01N-solution is given by the equation—

$$E = 0·528 \times 2 \times 0·0571 \log_{10} \frac{\gamma c_1}{a_2}$$

where γ is the activity coefficient of silver nitrate in 0·1N-solution (0·72). Since the activity coefficient of silver nitrate in 0·01N-solution is 0·90, a_2 should be equal to 0·0090. The calculated value of E is 0·0544 volt.

If a 3N-solution of potassium or ammonium nitrate is used as a salt-bridge between the two solutions of silver nitrate, the diffusion potential is practically eliminated, and the activity of silver ions in the 0·01N-solution is given by $E = 0·0571 \log_{10} \dfrac{0·072}{a_2}$.

Applications.—

1. *Solubility of Sparingly Soluble Salts.*—The following experiment will illustrate the application of measurements of the e.m.f. of concentration cells to the determination of the solubility of sparingly soluble salts.[1]

EXPERIMENT.—*Determine the Solubility of Silver Chloride in Water.*

Fit up the following cell—

$$\text{Ag} \quad \text{AgCl, 0·01N-KCl} \quad \begin{array}{c} \text{Sat. soln.} \\ \text{of NH}_4\text{NO}_3 \end{array} \quad \text{0·01N-AgNO}_3 \quad \text{Ag.}$$
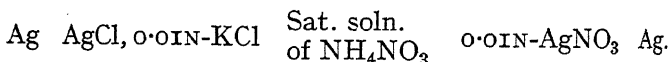
The silver electrodes are prepared as in the previous experiment. To the solution of 0·01N-KCl, surrounding one
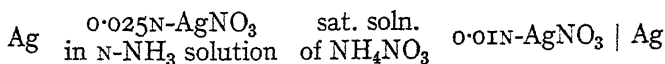
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[1] See Goodwin, *Z. physikal. Chem.*, 1894, **13**, 577; Abegg and Cox, *ibid.*, 1903, **46**, 1.

electrode, one or two drops of a silver nitrate solution are added, in order to give a precipitate of silver chloride. A saturated solution of silver chloride in 0·01N-KCl is thus obtained. Determine, at the room temperature (say 15°), the e.m.f. of the cell in the manner described above.

Calculation.—The concentration c of silver ions in the 0·01N-KCl, can be calculated by means of the expression $E = 0·0571 \log_{10} \dfrac{0·0090}{c}$, where E is the e.m.f. of the cell. Further, the concentration of chloride ions in this solution is equal, approximately, to 1×10^{-2}, or more accurately, to $0·92 \times 10^{-2}$ g.-equiv. per litre. By multiplying the concentration of silver ion, c, in the saturated solution by the concentration of chloride ion (1×10^{-2} or $0·92 \times 10^{-2}$) one obtains the value of the solubility product, K_s. Since, in pure aqueous solution, the concentration of the silver ions is equal to the concentration of the chloride ions, it follows that the concentration of either is equal to $\sqrt{K_s}$. Further, if it is assumed that the silver chloride at this dilution is completely ionized, then $\sqrt{K_s}$ also gives the concentration of silver chloride in the solution, *i.e.* the solubility. (The solubility at $18° = 1·09 \times 10^{-5}$ g.-equiv. per litre).

2. *Stability Constants of Complex Ions.*—When, for example, a silver salt is dissolved in a solution of ammonia, there is formed the complex ion $Ag(NH_3)_2^{\cdot}$. This ion undergoes a partial dissociation in accordance with the expression $Ag(NH_3)_2^{\cdot} \rightleftarrows Ag^{\cdot} + 2NH_3$. The greater the extent of this dissociation, the less stable is the complex ion, and the equilibrium constant, $K = [Ag^{\cdot}] \times [NH_3]^2 / [Ag(NH_3)_2^{\cdot}]$, is known as the " instability constant." The reciprocal of this expression is the " stability constant." Its value may be obtained from measurements of the e.m.f. of a concentration cell.
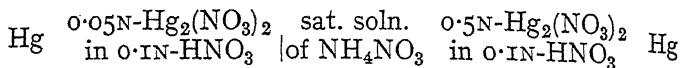
EXPERIMENT.—*Determine the E.M.F. of the following Cell.*[1]—

$$\text{Ag} \quad \begin{array}{cc} \text{0·025N-AgNO}_3 & \text{sat. soln.} \\ \text{in N-NH}_3 \text{ solution} & \text{of NH}_4\text{NO}_3 \end{array} \quad \text{0·01N-AgNO}_3 \mid \text{Ag}$$

and calculate therefrom the concentration of silver ion in the ammonia solution. The concentration of the complex ion may be taken as $0·025 \times 0·9$. Calculate the value of the " instability constant " of the complex ion.

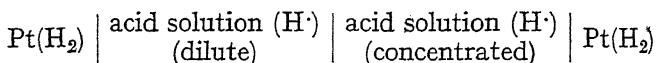[1] Bodländer and Fittig, *Z. physikal. Chem.*, 1902, **39**, 597; von Euler, *Ber.*, 1903, **36**, 1854.

3. *Valency of Metal Ion.*—By measuring the e.m.f. of the cell [1]—

$$\text{Hg} \quad \begin{array}{c} \text{0·05N-Hg}_2(\text{NO}_3)_2 \\ \text{in 0·1N-HNO}_3 \end{array} \Big| \begin{array}{c} \text{sat. soln.} \\ \text{of NH}_4\text{NO}_3 \end{array} \Big| \begin{array}{c} \text{0·5N-Hg}_2(\text{NO}_3)_2 \\ \text{in 0·1N-HNO}_3 \end{array} \quad \text{Hg}$$

the valency z of the mercurous ion can be determined by means of the expression, $E = \dfrac{0·058}{z} \log_{10} \dfrac{0·5}{0·05}$.

The Hydrogen Electrode.—In the case of the cells so far discussed, the reversible electrodes consisted of metals, in the solid or liquid (*e.g.* mercury) form, in electrical equilibrium with their ions in solution. It is, however, also possible to obtain reversible electrodes even in cases where the ion-forming element is a gas under ordinary conditions. Thus, a platinum electrode surrounded by hydrogen or by chlorine gas, and partly immersed in an electrolyte solution containing hydrogen ion or chloride ion, and saturated with the gas, acts as a reversible hydrogen or chlorine electrode. The potential of these electrodes depends on the concentration of $H^{\cdot}$ or of Cl' in the solution, as well as on the pressure of the gas around the electrode (or the concentration of the gas in the solution). Of such gas electrodes, as they are called, the hydrogen electrode is the most important, and a number of experiments may therefore be carried out with it.

For a cell of the type—

$$\text{Pt(H}_2) \Big| \begin{array}{c} \text{acid solution (H}^{\cdot}) \\ \text{(dilute)} \end{array} \Big| \begin{array}{c} \text{acid solution (H}^{\cdot}) \\ \text{(concentrated)} \end{array} \Big| \text{Pt(H}_2)$$

the e.m.f. will be given by the equation (p. 213)—

$$E = \frac{2 \cdot u_a}{u_c + u_a} \times 0·058 \log_{10} \frac{a_1}{a_2}$$

for temperatures between 15° and 20°. Whereas, in the cases previously studied, the value of $\dfrac{u_a}{u_c + u_a}$ was but little different from 0·5 (cf. the silver ion concentration cell), the value of this ratio in the case of acid solutions approximates more nearly to 0·2, on account of the fact that the mobility of $H^{\cdot}$ is very much greater than that of any anion.

[1] Ogg, *Z. physikal. Chem.*, 1898, **27**, 285 ; Linhart, *J. Amer. Chem. Soc.*, 1916, **38**, 2356. For similar determinations of the valency of tellurium, see Kasarnowsky, *Z. anorgan. Chem.*, 1923, **128**, 17.

Calculating the value of the e.m.f. of the cell—

$$Pt(H_2) \mid \text{0·01N-HCl} \mid \text{0·1N-HCl} \mid Pt(H_2)$$
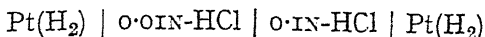
one obtains, for temperatures between 15° and 20°—

$$E = 0·17 \times 2 \times 0·058 \log_{10} \frac{\gamma_1 c_1}{\gamma_2 c_2}$$
$$= 0·17 \times 2 \times 0·058 \log_{10} 8·81$$
$$= 0·019 \text{ volt.}$$

By introducing between the two halves of the cell a saturated solution of potassium chloride, the diffusion potential can be to a large extent eliminated and the e.m.f. of the cell then becomes $E = \dfrac{2·303RT}{F} \log_{10} \dfrac{\gamma_1 c_1}{\gamma_2 c_2}$, or, at the mean temperature (15°–20°), $E = 0·058 \log_{10} \dfrac{\gamma_1 c_1}{\gamma_2 c_2}$.

EXPERIMENT.—*Determine the E.M.F. of a Hydrogen Concentration Cell.*

Preparation of the Electrodes.—As electrodes, oblong strips of platinum foil may be used. The foil is welded to a piece of platinum wire, which is then sealed into a glass tube ; and electrical connection with the outside circuit is made with the help of a small quantity of mercury. In order to obtain constant values of potential between electrode and solution, it is necessary or, at least, advisable, to coat the electrode with platinum black. This is best done electrolytically in the manner described on p. 161. Further, since the amount of hydrogen absorbed will depend on the thickness of the coating, care should be taken that the deposits on the two electrodes to be used in the concentration cell are as nearly as possible the same. The current used in platinizing the electrodes should therefore pass for equal times in each direction.

Before the electrodes are platinized, they should be cleaned by treatment for 5 minutes with a warm solution of potassium dichromate acidified with sulphuric acid, and then well washed with distilled water. After being platinized, the electrodes may be freed from occluded chlorine by immersion for a quarter of an hour in a mixed solution of ferrous and ferric salts acidified with sulphuric acid. They are then thoroughly washed with distilled water, and kept in distilled water till required for use.

The Electrode Vessel.—A convenient form of electrode

vessel is shown in Fig. 94. The platinum electrode E is fixed in the tube A by means of a rubber stopper and is partially immersed in the solution. Hydrogen gas is passed in through B and escapes through D and the mercury trap F. (See also p. 223.)

The hydrogen used should be pure. Hydrogen prepared electrolytically is best, but one may also use hydrogen prepared by the action of pure hydrochloric acid on zinc.[1] The gas should be passed through a solution of alkaline pyrogallate, and a solution of hydrochloric acid of the same concentration as is contained in the electrode vessel. The gas may be allowed to pass through the electrode vessel for
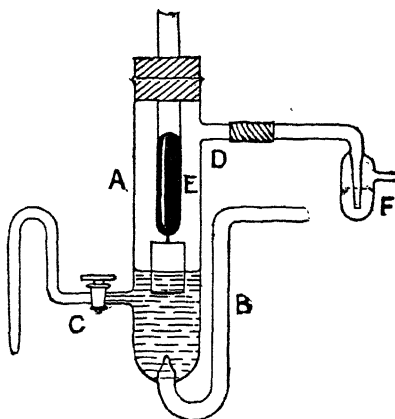
FIG. 94.

5–10 minutes, and the electrodes then allowed to remain surrounded by the gas for some time. This operation must be repeated, if necessary, until constant e.m.f. readings are obtained.

Two electrodes are prepared as described above, one containing deci-normal and the other centi-normal hydrochloric acid. They are then combined together into a cell by placing the ends of the side-tubes C in a o·IN-solution of HCl, contained in a beaker (see Fig. 93, p. 209). While measurements are being made, the passage of the hydrogen is stopped and the stop-cocks on the side-tubes C opened.

As the e.m.f. of this cell is small (see p. 217), it will be

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[1] For the purposes of routine measurements the hydrogen supplied commercially in cylinders will generally prove sufficiently pure.

necessary to combine it either in series with or in opposition to the standard cell. Measurements of the e.m.f. should be made from time to time, say every quarter of an hour, until the e.m.f. is constant. The slow passage of hydrogen through the cell should be continued meanwhile.

The value of the e.m.f. thus found should be compared with the theoretical value (p. 217). For the deci-normal solution, the value of γ may be taken as 0·81, and for the centi-normal solution, γ may be taken as 0·92.

The e.m.f. of the above concentration cell may also be determined using a saturated solution of KCl as a " salt-bridge," and so eliminating the liquid junction potential (see p. 204).

It is clear that if the concentration (or activity) of hydrogen ions at one electrode is known, the concentration (or activity) at the other electrode can be calculated.

Oxidation-Reduction Potentials.—When a metal is placed in a solution of one of its salts, there is established, as already learned, a certain electrode potential, which measures the tendency of the metal to pass into the ionic state, or of ions to pass into the atomic state. In other words, the electrode potential is a measure of the affinity of an atom for electricity.

Similarly, when platinum is immersed in a solution of a ferrous or ferric salt, or of some other reducing or oxidizing agent, a certain potential will be established depending on the affinity of the ions for electricity or their tendency to pass from a higher to a lower state of oxidation. If, for example, one sets up a cell of the type, $Pt \mid Fe^{\cdot\cdot} \parallel Fe^{\cdot\cdot\cdot} \mid Pt$, then on joining the two electrodes by a conductor, the ferrous ions will give up electrons to the electrode and thereby pass into the ferric state. The electrons flow along the connecting wire and are taken up by the ferric ions, which thereby pass into the ferrous state. The equilibrium state will be attained when the ratio of the activities of ferric and ferrous ions, or $a_{Fe^{\cdot\cdot\cdot}}/a_{Fe^{\cdot\cdot}}$, is the same at the two electrodes.

When a platinum electrode is placed in a solution containing ferric and ferrous ions, the potential of the electrode is given by the expression $E = E_0 + \dfrac{2 \cdot 303RT}{zF} \log_{10} \dfrac{a_{Fe^{\cdot\cdot\cdot}}}{a_{Fe^{\cdot\cdot}}}$, where z is the difference in valency of the ions and $a_{Fe^{\cdot\cdot\cdot}}$ and $a_{Fe^{\cdot\cdot}}$ are the activities of the ferric and ferrous ions respectively. Since $z = 1$, the above expression becomes, for

the temperature of $15°$, $E = E_0 + 0.0571 \log_{10} \dfrac{a_{Fe\cdots}}{a_{Fe\cdot\cdot}}$; or, since the ferric and ferrous salts may be regarded as having the same activity coefficient, one may use concentrations in place of activities and write $E = E_0 + 0.0571 \log_{10} \dfrac{[Fe\cdots]}{[Fe\cdot\cdot]}$. E_0 is the potential which is established when a platinum electrode is dipped in a solution in which the concentrations or activities of ferric and ferrous ions are the same. It is a measure of the tendency of the ion to pass from the higher to the lower state of oxidation. The more positive the value of the oxidation-reduction potential, the more effective is the ion in the higher state of oxidation as an oxidizing agent; and the more negative the oxidation-reduction potential, the more powerful is the ion in the lower state of oxidation as a reducing agent.[1]

EXPERIMENT.—*Determine the Oxidation-Reduction Potential of a Solution of Ferrous and Ferric Ions.*

Make up approximately $0.02M$ solutions of ferrous and ferric nitrate in $0.02N$ solutions of nitric acid (to diminish hydrolysis), and mix the solutions in approximately equal volumes. Analyse the mixed solution so as to ascertain the concentration of ferrous and ferric salt respectively, and introduce the solution, along with a platinum electrode, into a half cell (p. 205). Combine this with a normal calomel electrode, as shown in Fig. 93, p. 209, using a saturated solution of KCl in the middle vessel, and measure the e.m.f. of the combination. From this obtain the electrode potential as compared with the calomel electrode, and calculate the value of E_0. The ferrous and ferric salts may be regarded as having the same activity coefficient. It is customary to refer oxidation-reduction potentials to the potential of the normal hydrogen electrode. To the value of the potential referred to that of the normal calomel electrode as zero, one must therefore add algebraically $+0.2812$ volt, at $25°$. The value of E_0 for the ferric-ferrous electrode is $+0.743$, referred to the normal hydrogen electrode as zero.[2]

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[1] See also Gerke, *Chem. Reviews*, 1925, **1**, 377; Clark, *ibid.*, 1925, **2**, 127; Conant, *ibid.*, 1926, **3**, 1; Michaelis, *Oxidation-reduction Potentials.*
[2] For determinations of the value of E_0 ($+0.77$ volt), taking into account ionic strength, activity coefficients, etc., see Schumb and Sweetser, *J. Amer. Chem. Soc.*, 1935, **57**, 871.

Before use in the above experiment, the platinum electrode should be platinized (p. 217), and then alternately made the anode and cathode in a solution of sulphuric acid.

One may also study the oxidation-reduction potential of per manganate in sulphuric acid solution, and the variation of the potential with the acid concentration. Oxidation by permangan te takes place in accordance with the equation: $MnO'_4 + 8H\cdot + 5\ominus = Mn\cdot\cdot + 4H_2O$. The electrode potential, therefore, will be given by the expression: $E = E_0 + \dfrac{2\cdot303RT}{5F}\log_{10}\dfrac{[MnO'_4][H\cdot]^8}{[Mn\cdot\cdot]}$, where concentrations are put in place of activities. The potential, therefore, will vary markedly with the concentration of hydrogen ion, but for a given hydrogen ion concentration, it will depend on the ratio $[MnO'_4]/[Mn\cdot\cdot]$. When the hydrogen ion concentration is 1N, the potential $E_0 = +1\cdot446$.

The oxidation-reduction potentials of ferrocyanide-ferricyanide solutions and of stannic-stannous solutions in presence of acid may also be studied.

APPLICATIONS OF ELECTROMOTIVE FORCE MEASUREMENTS

I. HYDROGEN ION CONCENTRATION AND pH

Very many processes and reactions—chemical, biological and industrial—are more or less markedly influenced by hydrogen ion, and it is a matter of great importance to be able not only to determine the concentration of hydrogen ion in a solution but also to ensure that the medium possesses and maintains a definite and constant hydrogen ion concentration.

Formerly, the concentration of hydrogen ion in a solution was usually stated in terms of normality, or number of gram equivalents per litre and for concentrations less than normal was expressed in the form 1×10^{-n} normal. Hydrogen ion concentrations, however, are now very frequently expressed in terms of what is called the hydrogen ion exponent, a number obtained by giving a positive value to the negative power of 10 in the expression 1×10^{-n} normal, and represented by pH. The relation between the pH of a solution and the hydrogen ion concentration expressed in g.-equiv. per litre is given by the expression,[1] $p\mathrm{H} = \log_{10}\dfrac{1}{[H\cdot]}$, where $[H\cdot]$ is the concentration of hydrogen ions.

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[1] Representing concentrations in the form $[H\cdot] = 1 \times 10^{-n}$ normal, one obtains, on taking logarithms, $\log_{10}[H\cdot] = -n$, or $-\log_{10}[H\cdot] = n$. In accordance with what is said above, $p\mathrm{H} = n$, and hence $p\mathrm{H} = -\log_{10}[H\cdot]$ $= \log_{10}\dfrac{1}{[H\cdot]}$. For table of pH values, see Appendix.

Since the concentration, expressed in gram-equivalents per litre, is the reciprocal of the dilution, or number of litres in which 1 gram-equivalent is contained, one may also write $pH = \log_{10} v$. That is, the pH value of a solution is equal to the logarithm of the number of litres of solution which contain 1 gram of hydrogen ion.

Buffer Solutions.—To ensure constancy of pH, use is made of what are known as buffer solutions.

When, for example, one adds a small quantity of hydrochloric acid to a mixture of acetic acid and sodium acetate, the hydrogen ions unite to a large extent with acetate ions to form un-ionized acetic acid, and the concentration of hydrogen ion is thereby prevented from increasing to any considerable extent. Similarly, when a small quantity of alkali is added to the mixture, the hydroxide ions react with the acetic acid to form acetate ions and water, and again the hydrogen ion concentration remains unchanged.

For use in the experiments to be discussed in this chapter, the following buffer solutions, having different pH values, should be prepared : [1]—

pH = 3.   20·55 ml. M/5 Na$_2$HPO$_4$ + 79·45 ml. M/10 citric acid.
pH = 4.   41·0 ml. M/5 acetic acid + 9·0 ml. M/5 sodium acetate.
pH = 5.   14·75 ml. ,,   ,,   + 35·25 ml. ,,   ,,   ,,
pH = 6.   9·0 ml. ,,   ,,   +191·0 ml. ,,   ,,   ,,
pH = 7.   12·0 ml. M/20 borax   +188·0 ml. of a solution containing
                                                    12·40 g. H$_3$BO$_3$ and
                                                    2·93 g. NaCl in 1
                                                    litre.
pH = 8.   11·0 ml. ,,   ,,   + 29·0 ml.   ,,   ,,
pH = 9.   40·0 ml. ,,   ,,   + 10·0 ml.   ,,   ,,
pH = 9·24. Solution of M/20 borax.

Since the dissociation constants of ammonium hydroxide and acetic acid are identical, solutions of ammonium acetate constitute valuable neutral buffer solutions with pH = 7·0, and the pH remains constant over a wide range of concentrations.[2] The solutions should not be prepared from the salt but by mixing together equal volumes of accurately prepared 2N-solutions of ammonium hydroxide and acetic acid. Dilution of this normal solution does not alter the pH.

Determination of Hydrogen Ion Concentration.—For the electrometric determination of the concentration of hydrogen ions in a solution, various methods may be used. The more important of these will be described here.

[1] For the composition of different buffer solutions, see Clark, *The Determination of Hydrogen Ions* ; Britton, *Hydrogen Ions*.
[2] Williams and Lyman, *J. Amer. Chem. Soc.*, 1932, **54**, 1911 ; Schollenberger, *ibid.*, 2568.

Hydrogen Electrode.—It has already been shown that the concentration of hydrogen ions in a solution can be determined by means of a hydrogen ion concentration cell (p. 216). The potential of a hydrogen electrode depends on the concentration of hydrogen ion in the solution, and this concentration can be determined by combining a hydrogen electrode with a standard calomel electrode and measuring the e.m.f. of the combination.

As hydrogen electrode one may use the vessel shown in Fig. 94, p. 218, or the simpler form due to Hildebrand, shown in Fig. 95.[1]

The platinum wire from the electrode is sealed into the end of a glass tube B, which, in turn, is sealed near its upper end into a wider tube A.[2] Connection between the electrode and the rest of the voltaic circuit can be made by means of a copper wire dipping into mercury in tube B. The electrode is prepared as previously described (p. 217), and a current of hydrogen passed in through the side tube C, while the lower, expanded end of A is dipped in the acid solution. The hydrogen escapes through the holes a, a, so arranged that the platinum electrode is partially immersed in the liquid and partially surrounded by gas. The acid solution is connected by an inverted U-tube, filled with a saturated solution of KCl, with a solution of KCl into which the tube of an N-calomel electrode dips. Hydrogen is passed until the hydrogen electrode has acquired its equilibrium potential, and the voltage of the combination is then measured by one of the methods already described (pp. 199, 201, 202).
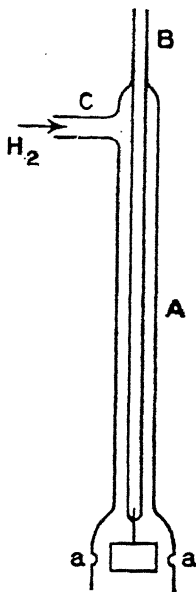
FIG. 95.

Since the diffusion potential is (practically) eliminated by the insertion of the saturated KCl solution, the potential of the hydrogen electrode referred to that of the normal hydrogen electrode is obtained by subtracting from the

[1] Many different forms of hydrogen electrode vessels have been described, specially adapted for various purposes. See Clark, *loc. cit.*

[2] It is in many ways more convenient that B should be fixed into A by means of a rubber stopper, as the electrode can then easily be removed and cleaned.

measured e.m.f. of the above cell, in which the normal calomel electrode is used, 0·2836 volt, which is the value at 15° of the calomel electrode potential referred to the normal hydrogen electrode. Taking, therefore, the potential of the normal hydrogen electrode as zero, the potential of a hydrogen electrode in contact with a solution which is h-normal in respect of hydrogen ions, is given by the expression—

$$E = \frac{2\cdot303RT}{F} \cdot \log_{10}\frac{1}{h} = 0\cdot0001983\ T \cdot \log_{10}\frac{1}{h}.$$

The concentration of hydrogen ions in a solution can therefore be calculated from measurements of the e.m.f. carried out as above by means of the expression—

$$\frac{\text{e.m.f. (measured)} -0\cdot2836}{0\cdot0571} = \log_{10}\frac{1}{h} = p\text{H (at 15°).}$$

From this expression it may be calculated that in a neutral solution ($h = 1 \times 10^{-7}$ or $p\text{H} = 7$), the e.m.f. of the cell

$$\text{Pt(H}_2) \quad \begin{matrix}\text{solution} \\ p\text{H}=7\end{matrix} \quad \begin{matrix}\text{saturated} \\ \text{KCl}\end{matrix} \quad \text{N-calomel electrode, at the}$$

mean temperature, 15°, will be 0·6833 volt.

Instead of using a calomel electrode with N-KCl solution and inserting a saturated solution of KCl to eliminate the diffusion potential, one may also, in the above experiment, employ a calomel electrode with saturated solution of KCl. In this case the insertion of a special intermediate solution of KCl is rendered unnecessary, and the side-tube of the calomel electrode may be immersed directly in the acid solution. The potential of the calomel electrode with saturated solution of KCl, referred to the normal hydrogen electrode as zero, is +0·2498 volt at 15°, and +0·2460 volt at 20°. At 15°, therefore,

$$p\text{H} = \frac{\text{e.m.f. (measured)} -0\cdot2498}{0\cdot0571}$$

It should be noted that the determinations of e.m.f. give the effective concentration of hydrogen ion, or the activity, expressed in gram ions per litre.

The hydrogen electrode, which has an accuracy, at constant temperature, of 0·02 $p\text{H}$, should not be used in the presence of oxidizing agents, of metals which lie below

hydrogen in the electromotive series (*e.g.* copper, silver), or of organic compounds which undergo hydrogenation. It is unsuitable for use, also, in presence of colloids.

EXPERIMENT.—*Determine the Concentration of Hydrogen Ions in a given Solution.*

For this measurement an approximately centinormal or milli-normal solution of hydrochloric acid may be used. One may also use one of the buffer solutions mentioned on p. 222, or a solution consisting of 50 ml. of 0·2M-KCl+6·7 ml. of 0·2M-HCl diluted to 200 ml. with conductivity water. The concentration of hydrogen ion in this solution is $6·31 \times 10^{-3}$ normal ; or $p\mathrm{H}=2·20$.

The Antimony Electrode.—Just as the hydrogen electrode is regarded as being in equilibrium with hydrogen ions in solution, so an oxygen electrode might be regarded as being in equilibrium with negatively charged oxygen ions (O''), formed in the reversible process, $2\mathrm{OH}' \rightleftharpoons \mathrm{O}'' + \mathrm{H}_2\mathrm{O}$. The potential of an oxygen electrode would therefore depend on the concentration of hydroxide ions in a solution; and since, in aqueous solutions, the product of concentrations of hydrogen ions and hydroxide ions is constant, at a constant temperature, the potential of the oxygen electrode would depend on the concentration (or activity) of hydrogen ions in the solution.

Although it appears that the oxygen gas electrode is not strictly reversible, a metal electrode in contact with its oxide may be regarded as a reversible oxygen electrode with the gas at a pressure equal to the dissociation pressure of the oxide. Thus antimony in contact with its oxide, $\mathrm{Sb}_2\mathrm{O}_3$, behaves as a reversible electrode, the potential of which is given by the expression,[1]

$$E = E_0 - \frac{2·303RT}{F} \log_{10} a_{\mathrm{H}^{\cdot}} = E_0 + \frac{2·303RT}{F} p\mathrm{H}.$$

This straight-line relationship holds over the range $p\mathrm{H}=2$ to $p\mathrm{H}=8$, and the value of E_0 must be determined for each electrode. If the antimony electrode is to be used for $p\mathrm{H}$ values greater than 8, it must first be standardized in solutions of known hydrogen ion concentration. The antimony electrode may be used over a wide range of acid solutions and even of alkaline solutions containing oxidizing

[1] See Parks and Beard, *J. Amer. Chem. Soc.*, 1932, **54**, 856; Perley, *Ind. Eng. Chem. (Anal.)*, 1939, **11**, 316, 319.

agents. It is also of value for use in the presence of colloidal matter. Its accuracy, however, is not greater than 0·05 pH.

Before use, the antimony electrode [1] should be polished with fine emery cloth and rinsed with distilled water. Under these conditions, a film of antimony oxide rapidly forms on the surface of the metal. The electrode is placed directly in the solution under investigation and is combined with a calomel electrode containing either a saturated or a normal solution of potassium chloride. The e.m.f. of this combination may be determined with buffer solutions of
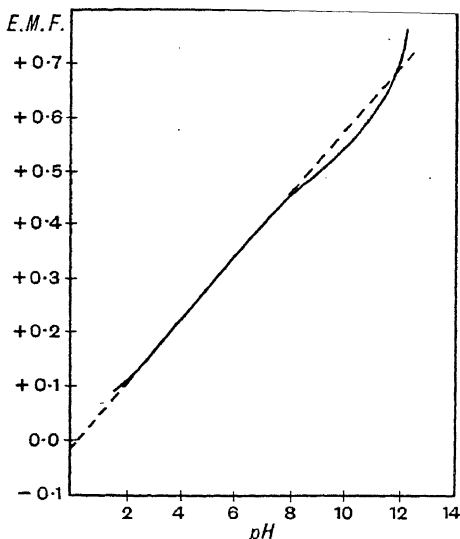
FIG. 96.

different known pH values between 2 and 11, and the values of e.m.f. are plotted against values of pH. The curve obtained is of the form shown in Fig. 96. By producing the straight portion of the curve to cut the e.m.f. axis, the value of E_0 in the above equation can be calculated, taking into account the potential of the calomel electrode (p. 206). In making the above measurements, the valve-potentiometer method (p. 201) should be used ; and the temperature also should be noted.

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[1] The antimony electrode may readily be prepared by casting molten antimony in a glass tube of about 6 mm. bore, and 6–10 cm. in length. A copper wire is soldered to one end to make electrical connections.

With the help of the e.m.f.—pH curve for a given antimony electrode, the pH of a solution can readily be obtained by determining the e.m.f. of the cell,

| Antimony electrode | Solution of unknown pH | Calomel electrode. |

The Quinhydrone Electrode.—For the determination of hydrogen ion concentration, use may also be made of the quinhydrone electrode, introduced by Biilmann.[1]   The use of this electrode depends on the fact that when quinone and hydroquinone are present together in a solution containing hydrogen ion, a reversible reaction takes place, represented by the equation :

$$C_6H_4O_2+2H^\cdot \;\rightleftarrows\; C_6H_6O_2-2\ominus$$
$$\text{Quinone (Q).} \qquad\qquad \text{Hydroquinone (QH}_2\text{).}$$
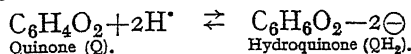
This is an oxidation-reduction reaction and the electrode potential at $18°$ is given by the equation

$$E=E_0+\frac{0\cdot0577}{2}\log_{10}\frac{[Q][H^\cdot]^2}{[QH_2]}$$
$$=E_0+\frac{0\cdot0577}{2}\log_{10}\frac{[Q]}{[QH_2]}+0\cdot0577\log_{10}[H^\cdot]$$

Therefore, when $[Q]=[QH_2]$, $E=E_0+0\cdot0577\log_{10}[H^\cdot]$.

This condition is satisfied when quinhydrone, a compound of one molecule of quinone with one molecule of hydroquinone, is dissolved in the solution.   In such a case, then, it is clear that the electrode potential changes with change in the concentration of hydrogen ion, in the same way as does the potential of the hydrogen electrode.

The value of E_0 has been found [2] to be $+0\cdot7181-0\cdot00074t$ volt, referred to the normal hydrogen electrode.   At $18°$, therefore, $E_0=0\cdot7048$.   If, therefore, the e.m.f. of a cell formed by a quinhydrone and a normal calomel electrode be measured, then, at $18°$,

$$E_{\text{observed}}=E_{\text{quinhydrone}}-E_{\text{calomel}}$$
$$=0\cdot705+0\cdot0577\log_{10}[H^\cdot]-E_{\text{calomel}}$$
$$\text{or, } -\log_{10}[H^\cdot]=p\text{H}=\frac{0\cdot705-E_{\text{calomel}}-E_{\text{observed}}}{0\cdot0577}$$
$$=\frac{0\cdot705-0\cdot283-E_{\text{observed}}}{0\cdot0577}$$

[1] *Ann. Chim.*, 1921, **15**, 109 ; *Bull. Soc. Chim.*, 1927, **41**, 151, 213. See also Lammert and Morgan, *J. Amer. Chem. Soc.*, 1932, **54**, 910 ; Morgan, Lammert and Campbell, *Trans. Amer. Electrochem. Soc.*, 1932, **61**, 199.
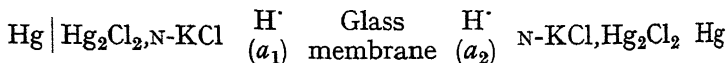[2] Harned and Wright, *J. Amer. Chem. Soc.*, 1933, **55**, 4849.

In carrying out a determination of the hydrogen ion concentration of a solution, about 1–2 grams of quinhydrone per 100 ml. of solution should be added and the solution well stirred.   (10–15 ml. of solution placed in a small beaker will suffice.)   A bright platinum electrode is immersed in the solution and combined into a cell with the normal calomel electrode, which forms the negative electrode of the cell. A saturated solution of potassium chloride is used as a salt-bridge ; or a calomel electrode with saturated KCl solution can be used in place of the normal calomel electrode. The e.m.f. of the cell is then determined.

Before use, the platinum electrode must be well cleaned by means of acid dichromate and washed with water.   It should then be heated to redness in an *alcohol*—not in a coal-gas—flame.

The quinhydrone electrode has, at constant temperature, an accuracy of about $0 \cdot 02 p$H.   It can be used in the presence of salts of metals which lie below hydrogen in the electromotive series, and with which, therefore, the hydrogen electrode cannot be used.   The quinhydrone electrode, however, cannot be used in presence of ammonium salts or with alkaline solutions which have a pH value greater than 8 ; that is, with solutions the hydrogen ion concentration of which is less than 1×10^{-8} normal.

The quinhydrone electrode is subject to " salt errors " when the concentration of electrolyte is greater than about $0 \cdot 1$M.   This defect can be overcome by saturating the solution not only with quinhydrone but also with quinone or hydroquinone.[1]   In the former case, $E_0 = 0 \cdot 7570$ volt and, in the latter case, $0 \cdot 6185$ volt, at $18°$.   It is advisable to have a small well at the bottom of the electrode vessel into which the solids settle and surround the platinum electrode.

The Glass Electrode.—The concentration of hydrogen ions in a solution may also be determined by means of the glass electrode, which is particularly useful in the case of oxidizing and reducing solutions, colloidal sols and biological fluids. Its use depends on the fact that when a glass surface is in contact with a solution it acquires a potential which depends on the concentration of the hydrogen ions in the solution. Thus, in the arrangement,

$$\text{Hg} \,|\, \text{Hg}_2\text{Cl}_2, \text{N-KCl} \quad \overset{\text{H·}}{(a_1)} \quad \overset{\text{Glass}}{\text{membrane}} \quad \overset{\text{H·}}{(a_2)} \quad \text{N-KCl}, \text{Hg}_2\text{Cl}_2 \,\, \text{Hg}$$

[1] Biilmann and Lund, *Ann. Chim.*, 1921, **16**, 321 ; Conant and Fieser, *J. Amer. Chem. Soc.*, 1923, **45**, 2194.

the e.m.f. depends on the concentrations (activities) of the hydrogen ions in the two solutions on either side of the membrane and is given by the expression,

$$E = K + \frac{2 \cdot 303 RT}{} \log_{10} \frac{a_2}{a_1},$$

where K is an " asymmetry potential " dependent on the nature of the glass, etc., and a_1 and a_2 are the hydrogen ion activities.

Owing to its liability to attack, the glass electrode is not suitable for use in highly alkaline solutions (pH $>$ 10).

Various forms have been given to the glass electrode, one of the most convenient being that due to C. Morton.[1] This consists of a thin-walled glass bulb, B, of high conductivity glass blown on the end of a tube of ordinary soda glass, D (Fig. 97). This is filled with N-HCl solution saturated with quinhydrone. A platinum wire connected with the terminal T_1 dips into the solution. The liquid, the

Fig. 97.

pH of which is to be determined, is introduced into the vessel A by means of the cup and tube H, and is connected with a calomel electrode, C. In this electrode a saturated solution of KCl is used in order to diminish the diffusion potential. The apparatus may be drained by means of the stop-cocks S, S_1, and the tubes E and F. During measurements, the stopcock S_1 is closed. Owing to the high resistance of the glass membrane, one should use a vacuum
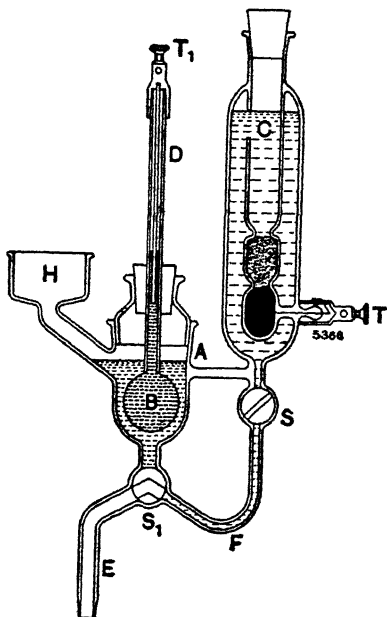
[1] *J. Sci. Inst.*, 1930, **7**, 187. Jena glass electrodes of very low internal resistance are now obtainable, and also electrodes constructed of a number of thin-walled glass tubes in place of the single bulb. Leeds and Northrup issue electrodes which are interchangeable, so that no re-calibration is required when changing from one to the other.

tube potentiometer.[1]   The electrode should be electrically screened by an earthed metal cage, and the wire leads sheathed in lead.

Before using the electrode for the determination of hydrogen ion concentrations, it is necessary first to calibrate the electrode by means of buffer solutions of known pH.   Thus, one measures the e.m.f. of two or three cells of the type:

a. Quinhydrone electrode	Glass membrane	Buffer solution $H^{\cdot} = a_1$	Calomel electrode
b. Quinhydrone electrode	Glass membrane	Buffer solution $H^{\cdot} = a_2$	Calomel electrode

and the e.m.f. is plotted against the pH values of the solutions.   This relationship is linear up to pH $= 10$.   The pH value of an unknown solution can then be determined by placing it in the vessel A and measuring the e.m.f.   The pH value can be read from the calibration curve.

EXPERIMENT.—*Investigate the Behaviour of a Buffer Solution.*

Prepare a centi-normal solution of acetic acid and dissolve in it an equivalent amount of solid sodium acetate.   Determine the pH of the solution, by means of one of the electrodes described in the preceding pages, and prepare a solution of acetic acid only of approximately the same pH.   To each of the solutions add, from a burette, definite small volumes of a solution of hydrochloric acid, and determine, in each case, the pH of the solution after each addition of acid. Plot the values of pH against the volume of acid added.

The investigation of the behaviour of different buffer solutions may be carried out.

The Activity of Hydrogen Ion and the Salt Effect.—The Arrhenius theory of ionization and the concept of degree of ionization, as measured by the ratio of equivalent conductivities, $\varLambda_c/\varLambda_0$, have, in the case of strong electrolytes, been displaced by the concept of activity, due to G. N. Lewis, and the theory of Debye and Hückel.   The term *activity* is

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[1] See, for example, Greville and Maclagan, *T. Faraday Soc.*, 1931, **27**, 210 ; *J. Chem. Soc.*, **1932**, 720 ; Morton, *J. Sci. Instr.*, 1932, **9**, 289 ; *Ann. Reports, Chem. Soc.*, 1933, **30**, 283 ; Bromley, *Analyst*, 1935, **60**, 533. Suitable apparatus is manufactured by the Cambridge Instrument Co., London, and by Leeds and Northrup, Philadelphia.

defined as that quantity which expresses the effect of a substance on an equilibrium when substituted for the concentration in the law of mass action. In the case of electrolytes, the activity coefficient may be determined in various ways, *e.g.* by measurement of the electromotive force of a cell, so that if the activity coefficient at one concentration is known, its value at another concentration may be calculated from measurements of electromotive force.

In the case of a strong binary electrolyte, the activities of the cation and anion may be represented by a_+ and a_- respectively, and if the activity of the undissociated solute be represented by a_2, there is obtained the equilibrium relation $\dfrac{a_+ a_-}{a_2} = K$. While the value of a_2 can, in some cases, be determined experimentally, it cannot be so in all cases ; and the activity of the undissociated molecules is defined by putting K, in the above expression, equal to unity. One then obtains $a_+ a_- = a_2$. At zero concentration $a_+ = a_-$, but as it is not certain up to what degree of concentration this equality holds, it is usual to consider merely the mean activity of the ions, $a_\pm$, which is defined as the geometrical mean of the activities a_+ and a_-. One then has, $a_\pm = \sqrt{a_+ a_-} = \sqrt{a_2}$.

The activity coefficient, represented by γ, which is analogous to the Arrhenius degree of dissociation, is defined as the mean activity of the ions divided by the molar concentration of the electrolyte, or $\gamma = \dfrac{a_\pm}{c}$.

If, in the Nernst equation, $E = \dfrac{RT}{zF} \cdot \log_e \dfrac{\alpha_2 c_2}{\alpha_1 c_1}$, the ionic concentrations are replaced by activities, one obtains the equations,

$$E = \frac{RT}{zF} \cdot \log_e \frac{a_2''}{a_2'} = \frac{RT}{zF} \log_e \frac{a_+'' \times a_-''}{a_+' \times a_-'}$$

where the single dash and the double dash refer to two different concentrations. But, $a_\pm = \sqrt{a_+ a_-} = \gamma \cdot c$, and therefore,

$$E = \frac{RT}{zF} \cdot \log_e \left(\frac{\gamma'' c''}{\gamma' c'} \right)^2 = \frac{2RT}{zF} \log_e \frac{\gamma'' c''}{\gamma' c'}$$

The former equations give the electromotive force in terms of the individual ion activities, a_+ and a_-, while the latter

equations give it in terms of the activity coefficients of the electrolytes. These equations should be substituted for the older Nernst equation.

By means of e.m.f. measurements, therefore, one can follow changes in the activity of an ion, and it is of interest to follow the change in the activity of hydrogen ion produced by the addition of a neutral salt. This is known as the *salt effect*.

When a metal chloride, *e.g.* KCl, is added to a solution of hydrochloric acid, the law of mass action would indicate that the concentration of the hydrogen ion, and therefore its activity, is diminished. From measurements of the hydrogen electrode potential, however, it has been found that this is not always the case. Addition of a neutral salt to the acid may increase the ionic activity of the hydrogen ion.

EXPERIMENT.—*Determine the Influence of Salts on the Activity of Hydrogen Ion.*

The apparatus is fitted up as for the determination of hydrogen ion concentration, the cell, the e.m.f. of which is to be measured, being of the type :

$$\text{Pt(H}_2)\quad \text{acid}\quad \begin{array}{c}\text{saturated}\\\text{KCl solution}\end{array}\quad \begin{array}{c}\text{N-calomel}\\\text{electrode}\end{array}$$
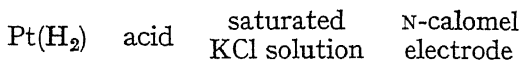
A definite volume, say, 50 ml. of 0·01N-HCl is placed in a beaker, and the cell formed as above. Determine the e.m.f. of the cell. Then add to the hydrochloric acid successive amounts of potassium chloride or sodium chloride, so that the total amount of salt added varies from about 0·2 to 6·0 grams. After each addition of salt, determine the e.m.f.

From each measurement made, calculate the pH value of the solution (p. 224), and plot these values against the concentration of salt, expressed in gram-molecules per litre.

From the values of the activity coefficients of hydrochloric acid at different concentrations (see Appendix), the activity of hydrogen ion in the pure acid solution used can be obtained (on the assumption that the activities of the hydrogen ion and chloride ion are equal). This value, a_0, is then inserted in the equation, $E_0 - E_s = \dfrac{2 \cdot 303 RT}{F} \log_{10} \dfrac{a_s}{a_0}$, and the activity of the hydrogen ion in presence of salt (a_s) is calculated. E_0 is the e.m.f. of the cell when pure acid is

used, and E_s the e.m.f. when a definite amount of salt has been added to the acid. Plot the values of the hydrogen ion activity against concentration of salt.

Carry out similar determinations and calculations with solutions of sulphuric acid to which sodium sulphate or potassium sulphate is added, and with solutions of acetic acid to which sodium acetate is added.

Hydrolysis of Salts.—The degree of hydrolysis of the salt of a weak acid or weak base can, as has been shown (p. 186), be determined by conductivity measurements. It can also, and more satisfactorily, be determined by potentiometric methods, which enable one to determine, more directly, the concentration of hydrogen or hydroxide ions in the solution.

If aniline hydrochloride, for example, is dissolved in water, and if x is the degree of hydrolysis, the concentration of free base and of free acid will be $x \cdot c$, where c is the total concentration of the salt. As the hydrochloric acid may be regarded as completely ionized, the concentration of hydrogen ion will also be $x \cdot c$. Therefore, if one determines by the potentiometric method, the concentration of hydrogen ion in the solution of aniline hydrochloride, one obtains directly the value $x \cdot c$. From this, knowing the value of c, one can calculate x.

Solutions of aniline hydrochloride of different concentrations ($N/32$, $N/64$, $N/128$) are prepared,[1] and the concentration of hydrogen ion determined by means of a hydrogen and normal calomel electrode (p. 223), or by a quinhydrone and calomel electrode (p. 227).

Calculate the value of x, the degree of hydrolysis, and also the hydrolytic constant, from the equation $K_h = x^2 \cdot c/(1-x)$. Further, from the relationship, $K_h = K_w/K_b$, calculate the affinity constant of the base K_b, taking the value of K_w, the ionic product of water, as 0.46×10^{-14} at $15°$, and 0.59×10^{-14} at $18°$.

The hydrolysis of various metal salts, *e.g.* copper sulphate and nickel sulphate, may similarly be determined, using a quinhydrone electrode.

The determination of the degree of hydrolysis of salts of weak acids and strong bases (*e.g.* sodium acetate) may also be carried out, using a hydrogen electrode.

[1] By adding the proper amount of pure aniline to an $N/32$ solution of hydrochloric acid, and diluting with distilled water.

II. Potentiometric Titrations

Since the potential of an electrode dipping in the solution of an electrolyte depends on the concentration of the ions with which the electrode is in equilibrium, it is possible to use determinations of the potential as an " indicator " in volumetric analysis.   Thus, the cell

$$Pt(H_2) \mid Acid \ solution \mid KNO_3 \mid Calomel \ electrode$$

will have a certain e.m.f. depending on the concentration of hydrogen ion in the acid solution.   On adding a standard solution of alkali to the acid, the e.m.f. of the cell will alter
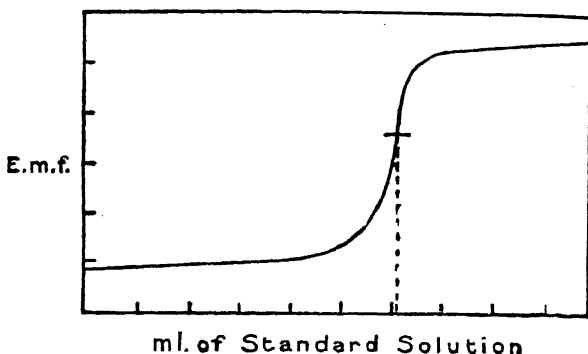
ml. of Standard Solution
Fig. 98.

slowly at first, because the change in the electrode potential depends on the *fractional* amount of hydrogen ion removed. As the amount of alkali added approaches equivalence to the amount of hydrogen ion in the solution, the fraction of the hydrogen ion concentration removed by each drop of alkali solution rapidly increases, and there is a correspondingly rapid change in the e.m.f.   Later, as excess of alkali is added, the e.m.f. again shows a slow change.   Consequently, when the e.m.f. of the cell is plotted against the volume of standard alkali added, a curve of the form shown in Fig. 98 is obtained.   The end-point of the titration is given by the point of inflection on the curve.[1]

In carrying out the titrations, the titrating liquid is run, in small quantities at a time, from a burette into the solution

[1] The point of inflection can be most easily found by plotting the values of $\Delta E/\Delta v$ against volume of titrating solution.   At the point of inflection the value of $\Delta E/\Delta v$ is a maximum.

to be titrated, the solution being kept well stirred by means of a stirrer. As the titration approaches the equivalence point, the titrating liquid is added in smaller and smaller amounts.

The variation of the e.m.f. of a cell during titration may be determined by the potentiometer-voltmeter method (p. 201), or, preferably, by the valve-potentiometer method (p. 201). In using the former method, values of e.m.f. are plotted against ml. of standard titrating solution added, and the point of inflection on the curve ascertained. In using the latter method, one may proceed as follows. After balancing out the anode current, with the switch S in position 1, the switch is placed in position 2, so as to place the titration cell in the grid-filament circuit ; and the resistance R_2 is adjusted so that the galvanometer is undeflected. A small

quantity of the titrating solution is then added and the galvanometer deflection noted. This deflection is again balanced out, a further quantity of titrating solution is added and the galvanometer deflection again noted. The deflection is again balanced out, and the procedure continued. The de-

ml. titrating solution

Fig. 99.

flections are plotted against the number of ml. of titrating solution added, when a curve of the form shown in Fig. 99 will be obtained. The point of maximum deflection occurs at the equivalence point.
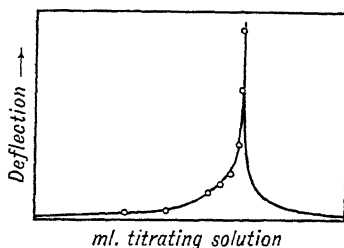
In the case of the valve-potentiometer method one can also, as already explained (p. 202), determine the e.m.f. of the titration cell, and these values can be plotted against ml. of titrating solution.

The method of potentiometric titration has found very varied and widespread application, and a number of the following experiments should be carried out.[1]

1. **Titration of Acid with Alkali.**—Cells should be set up as for the determination of hydrogen ion concentration (p. 222 ff.), and experiments may be made using different electrodes. Standard alkali solution is run into the acid, and the point

[1] See Furman, *Ind. Eng. Chem. (Anal.)*, 1930, **2**, 213 ; Glasstone, *Chem. Soc. Annual Reports*, 1933.

of equivalence ascertained in the manner described in the preceding pages. Neutralization experiments should be carried out with, say, hydrochloric acid, acetic acid (e.g. commercial vinegar) and a polybasic acid, such as chromic acid or phosphoric acid.[1] The results should be compared with those obtained by the ordinary methods of volumetric analysis.

Neutralization Curve.—The neutralization of a strong acid by a strong alkali, of a weak acid by a strong alkali, of a strong acid by a weak alkali, and of a weak acid by a weak alkali should be studied. Calculate, in each case, the pH of the solution after each addition of the titrating solution and plot the value of pH against the volume of titrating solution. Except in the last case, a curve will be obtained which shows a very steep portion corresponding to a large change in the pH value for small changes in the volume of titrating solution. Note in each case the pH value of the solution at the point of equivalence.

It is instructive to carry out these neutralization experiments in the presence of a drop or two of different indicators, and so to study their behaviour with different acids and alkalis. A solution of sodium carbonate may also be titrated with hydrochloric acid. Phenolphthalein is first added and when it becomes colourless methyl orange is added and the titration continued until the colour changes. Note in each case the volume of acid added and the pH of the solution when the indicators change colour.

Consider the use of different indicators in acid-alkali titrations (p. 244).

Affinity Constants of Weak Acids.—For mixtures of a weak acid and of a salt of the acid, the hydrogen ion concentration is given, approximately, by the expression $[H^{\cdot}] = K \cdot [acid]/[salt]$, where K is the affinity constant of the acid. From this it follows that $\log 1/[H^{\cdot}] = \log 1/K + \log [salt]/[acid]$, or pH$= \log 1/K + \log [salt]/[acid]$. This expression gives the variation of the pH value of the solution during neutralization, and it shows that when the acid is half neutralized, *i.e.* when $[salt] = [acid]$, pH$= \log 1/K$. If, therefore, one determines potentiometrically the variation of pH with neutralization, and if one plots the value of pH against the volume of standard alkali added, one can read off from the curve the value of pH corresponding to half neutralization, and calculate therefrom the value of K, the affinity constant of the acid.

[1] See Britton, *J. Chem. Soc.*, 1924, **125**, 1572 ; **1927**, 614.

The value of K may also, with greater accuracy, be calculated by means of the relation, $K=[\text{H}^{\cdot}]\times[\text{salt}]/[\text{acid}]$. After each addition of alkali to the titration cell, the value of the e.m.f. is determined, and the concentration of hydrogen ion in the solution, calculated. Since the concentration of salt in the solution will be proportional to the volume, x, of alkali added, and the concentration of acid to the quantity (x_e-x), where x_e is the volume of alkali required for complete neutralization of the acid, it follows that $K=[\text{H}^{\cdot}]\times\dfrac{x}{x_e-x}$. The mean of the different K-values is then taken.

EXPERIMENTS.—*Determine the affinity constants of various monobasic and polybasic acids, such as benzoic acid, acetic acid; succinic acid, tartaric acid; phosphoric acid, citric acid.*[1]

2. Precipitation Reactions.—A very large number of precipitation reactions may be followed by potentiometric measurements.[2] The following may be taken as examples.

EXPERIMENT.—*Titrate a Solution of Silver Nitrate.*

The solution of silver nitrate is placed in a beaker and in the solution is placed an electrode of silver wire or foil. A stirrer is fitted up so that the solution may be kept well stirred during the titration. By means of an inverted $\bigcup$-tube filled with a solution of NH_4NO_3 (the open ends of the tube being loosely plugged by means of well-washed cotton-wool or by sintered glass), the solution of silver nitrate is placed in connection with a concentrated solution of ammonium nitrate contained in a small beaker. Into this solution is placed the capillary end of the calomel electrode tube. The e.m.f. of this combination is then measured and the result noted. Into the silver nitrate solution, well stirred, a standard solution of NaCl is run, and after each addition the e.m.f. of the cell is determined. Plot the values of e.m.f. against volume of NaCl solution run in, and determine the point of inflection of the curve.

Titration without a Potentiometer.—A new method of titration of halides and of acids, which makes the use of a potentiometer unnecessary, has been suggested by B. Cavanagh.[3] If one has a hydrogen electrode and a silver chloride electrode dipping in a solution containing hydrogen ion and chloride ion, the e.m.f. of the cell, at $16°$, is given by

[1] See, for example, Morton, *T. Faraday Soc.*, 1928, **24**, 14.

[2] See Taylor, *Physical Chemistry*, Vol. II, Chap. 13; Kolthoff and Furman, *Potentiometric Titrations* (Wiley).

[3] *J. Chem. Soc.*, 1927, **142**, 2207; **1928**, 843, 855.

the expression, $E = E_0 + 0.05735 \log_{10}(C_{H\cdot} \times C_{Cl'})$. If silver nitrate is added to the solution, then at the titration end-point, the value of $C_{Cl'}$ will be equal to the solubility, S_{AgCl}, of silver chloride. At the titration end-point, therefore, the e.m.f. will be, $E = (E_0 + 0.05735 \log_{10}S_{AgCl}) + 0.05735 \log_{10}C_{H\cdot}$. Since, in this equation, the bracketed expression is constant, it follows that the end-point e.m.f. depends on the concentration of hydrogen ion. Similarly, if a solution of acid and chloride be titrated with a strong alkali, the value of $C_{H\cdot}$ at the end-point is equal to the acidity, h, of distilled water in presence of an atmosphere containing carbon dioxide, say, $2-3 \times 10^{-6}$ normal. We have, therefore, $E = (E_0 + 0.05735 \log_{10}h) + 0.05735 \log_{10}C_{Cl'}$.

Measurements made with cells containing various proportions and concentrations of hydrogen ion and chloride ion, gave, for E_0, in the more exact expression, $E = E_0 + 0.05735 \log_{10}a_H a_{Cl}$ (where a_H and a_{Cl} are the ion activities), the value, 0.4740 volt.

If, in the case of the chloride titration, one substitutes this value for E_0 and 0.97×10^{-5} for S_{AgCl}, one obtains, for the end-point potential, $E_{Cl} = 0.1866 + 0.05735 \log_{10}C_{H\cdot}$. Calculation shows that E_{Cl} becomes zero when $C_{H\cdot} = 5.6 \times 10^{-4}$; that is, if the acidity of the solution is roughly $N/1800$. By using a silver chloride and quinhydrone electrode, and connecting these two electrodes with a galvanometer, the end-point of the titration is found by noting the titration at which the deflection of the galvanometer changes direction.

Similarly, for acid-alkali titration, substituting the value for E_0 and for h (2.5×10^{-6}) one obtains for the end-point potential, $E_{H\cdot} = 0.153 + 0.05735 \log_{10}C_{Cl}$, which becomes zero when $C_{Cl} = 2.2 \times 10^{-3}(N/450)$.

EXPERIMENT.—*Titrate a Solution of Potassium Chloride.*

Place, say, 100 ml. of $N/400$-KCl in a conical flask and add such an amount of nitric acid as will make the solution approximately $N/1800$, and quinhydrone to the amount of 1 mg. per ml. of solution. Shake the flask, until most of the quinhydrone is dissolved. A stout silver wire, about 15 cm. long, is coated, along a length of about 5 cm. from one end, with silver chloride, by making it the anode in the electrolysis of a solution of sodium or potassium chloride and using a current of 2–3 milliamperes per sq. cm. This is used as the silver chloride electrode. A stout platinum wire, or platinum foil attached to platinum wire, is used as the

other electrode. These two electrodes mounted side by side dip into the above solution in the conical flask. The electrodes are connected, through a tapping key, with a pointer galvanometer (capable of detecting 10^{-7} amp.), in series with a rheostat. The resistance is regulated so as to make the galvanometer deflections small. Silver nitrate (N/100) is run into the solution from a burette, and after each addition, the tapping key is depressed and the galvanometer deflection noted, until a point is reached at which the *direction* of the deflection is reversed. This indicates that the e.m.f. of the cell has reached and passed zero. By plotting deflections [1] against volume of silver nitrate, the titration corresponding to zero e.m.f. can be obtained.

EXPERIMENT.—*Titrate a Solution of Acid.*

In a manner similar to that described above, a solution of acid can be titrated. A solution of nitric acid, say, N/400, is placed in the titration flask along with quinhydrone and sufficient NaCl or KCl to give a concentration, $C_{Cl} = N/450$. The solution is titrated with N/100-NaOH (free from carbonate) or with baryta. The titration end-point corresponding to zero e.m.f. is determined as above.

3. Oxidation-Reduction Reactions. — The change in the e.m.f. of a cell due to the variation of the oxidation-reduction potential of an electrode, makes it possible to follow oxidation-reduction reactions potentiometrically.

EXPERIMENT.—*Determine the Concentration of Ferrous Salt in a Solution.*

Set up the cell—

Pt | ferrous salt solution+acid | N-Calomel Electrode

and determine its e.m.f. by the method described on p. 199, or p. 201. Stir the ferrous solution and run in from a burette standard dichromate solution (say, N/20), and determine the e.m.f. of the cell, or the quantity $\Delta E/\Delta v$, after each addition. Plot the results and ascertain the point of inflection on the curve, or the point at which $\Delta E/\Delta v$ is a maximum. Read off the volume of dichromate solution corresponding to this point, and compare it with the amount found by the ordinary method of titration, using ferricyanide as indicator.

The effect of varying acid concentration on the form of the e.m.f. curve should also be studied.

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[1] In the neighbourhood of the end-point, the rheostat resistance should not be altered.

Platinum-Tungsten Electrodes.—In the case of oxidation-reduction reactions, potentiometric titration is greatly simplified by making use of the fact that when a platinum and a tungsten electrode are immersed in an oxidation-reduction solution, the platinum electrode indicates the reversible potential of the system, but the tungsten electrode does not do so. At the end-point of the titration, therefore, the potential of the platinum electrode changes suddenly, but that of the tungsten electrode remains unchanged.

The following arrangement is very convenient (Fig. 100).[1]

A dry cell, B ($1 \cdot 5$ volt) is connected with a milliammeter, A, through the rheostat R (1500 ohms), and the fuse wire F. The platinum and tungsten electrodes, immersed in the solution to be titrated contained in the beaker C, are connected to the points 1 and 2 of the switch S, so that the e.m.f. of the oxidation-reduction cell, C, is opposed to that of the dry cell, B. (Usually, the platinum electrode is the positive pole of the oxidation-reduction cell.) Switch S is first put in position 1 and the rheostat adjusted so that the ammeter shows the full deflection (100 divisions = 1 milliampere).
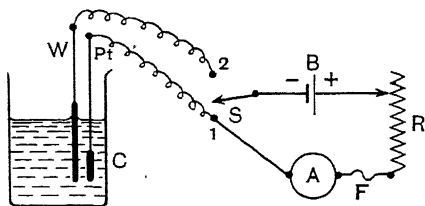
FIG. 100.

Switch S is then placed in position 2, and the ammeter reading noted.[2] The solution is vigorously stirred and the titrating solution added gradually from a burette, and drop by drop as one approaches the equivalence point. At this point the ammeter will show a sudden, large change in the deflection.

Plot the ammeter readings against volume of titrating solution and find the point of inflection.

Before use, the platinum electrode should be cleaned by means of chromic acid, rinsed with distilled water and ignited in an *alcohol* flame. The tungsten electrode should be polished with an emery cloth. When not in use, the electrodes are kept in a solution of chromic acid.

EXPERIMENTS.—1. Titrate an approximately $0 \cdot 4$N solution of potassium dichromate with $0 \cdot 2$N solution of ferrous ammonium sulphate. The dichromate solution should be acidified with sulphuric acid (5 ml. of concentrated sulphuric acid per 100 ml. of solution).

2. Titrate an approximately $0 \cdot 2$N solution of ferrous ammonium sulphate (acidified with sulphuric acid) with $0 \cdot 1$N solution of potassium permanganate.

4. Electromotive Force, Equilibrium and Free Energy.—Of the applications of e.m.f. measurements, the determinations of the decrease of free energy and of the equilibrium

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[1] Gay, *Ind. Eng. Chem. (Anal.)*, 1939, **11**, 383.
[2] If the ammeter pointer swings off-scale, it shows that the platinum-tungsten electrodes have been wrongly connected to points 1 and 2.

constant of a reversible electrolytic reaction are among the most important. The decrease of free energy is obtained directly from the e.m.f., E, of an appropriate voltaic cell, since $-\Delta F = z\mathbf{F}E$, where $z\mathbf{F}$ is the number of coulombs associated with 1 g.-mol. Moreover, by applying the van't Hoff isotherm, one obtains the expression $-\Delta F = \mathbf{R}T \log_e K -\mathbf{R}T \log_e x$, where x is the initial mass law ratio of activities of resultants and reactants, and K is the equilibrium constant. It follows, therefore, that

$$E = \frac{2 \cdot 303 \mathbf{R}T}{z\mathbf{F}} (\log_{10} K - \log_{10} x).$$

A convenient reaction by which one may study these relations is that represented by the equation, $TlCl + KSCNaq \rightleftharpoons TlSCN + KClaq$, which reaches an equilibrium state when the ratio of concentrations,[1] $[Cl']/[SCN'] = K$. In this case, the value of K can be calculated from the e.m.f. of the cell [2]—

Tl-amalgam|TlCl, KCl (sol.)||KSCN (sol.),TlSCN |Tl-amalgam
in which the ratio $[Cl']/[SCN'] = x$. When $x < K$, the positive current will flow in the cell from right to left, thereby causing an increase in the concentration of chloride ion and a decrease in the concentration of thiocyanate ion, and when $x > K$, the current will flow in the opposite direction.

Experimental.—Two half cells are prepared similar to those used for the calomel electrode (p. 204), containing, in the one case, thallium amalgam, solid thallium chloride and a solution of potassium chloride (0·08M), saturated with thallium chloride ; and, in the other case, thallium amalgam, solid thallium thiocyanate and a solution of potassium thiocyanate (0·1M), saturated with thallium thiocyanate. The thallium amalgam should have the same composition in the two halves of the cell.[3]   A 3M-solution of ammonium nitrate may be used as a salt-bridge. The e.m.f. of the combination is determined, using the valve potentiometer method (p. 201), and the value of the equilibrium constant is calculated from the expression given above, x having the

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[1] The use, in this case, of concentrations in place of activities introduces only a small error when the solutions are dilute.

[2] Knüpffer, *Z. physikal. Chem.*, 1898, **26**, 255.

[3] The thallium analgam should contain 1–2 per cent. of thallium.   It is best prepared by electrolysing a solution of thallium sulphate, containing the calculated amount of thallium, with a known weight of mercury as cathode.

16

value of 0·8.[1]　(At 25°, K was found electrometrically to be 1·27.)

Equilibrium by chemical analysis.—The chemical equilibrium may be determined by shaking, say, 200 ml. of 0·1N-KSCN with 10 g. of solid thallium chloride, or 200 ml. of 0·1N-KCl with 10 g. of solid thallium thiocyanate. To a portion of the equilibrium solution potassium hydrogen iodate and sulphuric acid are added in order to oxidize the thiocyanic acid to hydrocyanic acid, and the hydrocyanic acid and iodine liberated are driven off by boiling. The chloride remaining is then titrated with silver nitrate.

Another equal portion of the equilibrium solution is titrated with silver nitrate so as to give the total chloride plus thiocyanate. By subtracting from this total the amount of chloride present, one obtains the amount of thiocyanate. The equilibrium ratio [Cl]/[SCN] found by chemical analysis was 1·24.

Other determinations of the e.m.f. of the above cell may be made using other concentrations of potassium chloride and potassium thiocyanate. Determinations may also be made at different temperatures (say, 20°, 30°, 40°), using stoppered cells in a carefully regulated thermostat. These determinations of e.m.f. must be made with an accuracy of 0·01 millivolt.

Free Energy.—From the value of the equilibrium constant, one calculates the decrease of free energy of the reaction, TlCl+SCN′ =TlSCN+Cl′, to be, at 25°, $-\Delta F = 2 \cdot 303 RT \log_{10} K = 2 \cdot 303 \times 1 \cdot 987 \times 298 \log_{10} 1 \cdot 27 = 141 \cdot 6$ cal.

Heat of Reaction.—On determining the e.m.f. of the cell at different temperatures, the temperature coefficient of e.m.f. was found to be $-0 \cdot 00044$ volt per degree. The heat of reaction, at 20°, is, therefore,

$$-\Delta H = F\left(E - T\frac{dE}{dT}\right)$$
$$= 96,500 \ (0 \cdot 0105 + 293 \times 0 \cdot 00044) \ \text{volt-coul.}$$
$$= 3220 \ \text{cal.}$$

The value determined thermochemically is 3180 cal.

Further Determinations.—The equilibrium constant of the reaction, Fe···+Ag⇌Fe··+Ag·, may be calculated from the e.m.f. of the cell [2]:

Pt	0·025M-Fe(NO$_3$)$_3$ 0·075M-Fe(NO$_3$)$_2$ 0·05M-HNO$_3$	0·05M- HNO$_3$	0·05M-AgNO$_3$ 0·05M-HNO$_3$	Ag
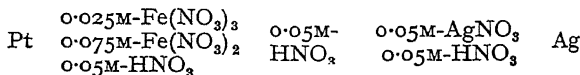
The ferrous nitrate is best obtained by mixing equivalent quantities of Ba(NO$_3$)$_2$ and FeSO$_4$.

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[1] The ratio of concentrations may be taken as being equal to the ratio of the activities.

[2] Noyes and Brann, *J. Amer. Chem. Soc.*, 1912, **34**, 1016.

The oxidation of hydroquinone by silver ions leading to the equilibrium, $C_6H_4(OH)_2+2Ag^{\cdot}\rightleftharpoons C_6H_4O_2+2Ag+2H^{\cdot}$, may be studied by means of the cell,[1]

Pt | Quinhydrone, o·1M-HNO$_3$ ‖ o·1M-HNO$_3$, o·001M-AgNO$_3$ | Ag
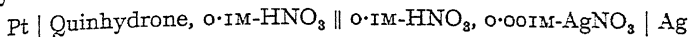
For the calculation of heat of reaction from e.m.f., one may study the cell formed by a cadmium (or cadmium amalgam) electrode and a silver-silver chloride electrode immersed in a saturated solution of CdCl$_2$, 2·5H$_2$O. The reaction involved is :[2] $Cd+2AgCl+2\cdot5H_2O=CdCl_2, 2\cdot5H_2O+2Ag$. It should, however, be remembered that such measurements are of little value unless the e.m.f. can be determined with an accuracy of about o·01 millivolt.

5. Determination of Transport Numbers.—The e.m.f. (E_t) of the concentration cell with transport,

$$Ag \mid AgCl, LiCl(a_1) \mid LiCl(a_2), AgCl \mid Ag,$$
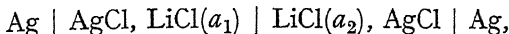
in which the electrodes are reversible with respect to chloride ion, is given by the expression, $E_t=\dfrac{2 \cdot u_c}{u_c+u_a} \cdot \dfrac{RT}{F} \log_e\dfrac{a_1}{a_2}$. If, however, a cell is constructed in which lithium amalgam is inserted between two solutions of lithium chloride, one obtains a concentration cell without transport, because lithium chloride is not transferred from one solution to the other when current is taken from the cell. Such a cell may be represented by the scheme

$$Ag \mid AgCl, LiCl(a_1) \mid Li(Hg)_x \mid LiCl(a_2), AgCl \mid Ag$$
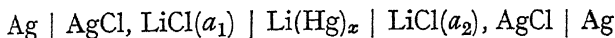
and may be regarded as consisting of two cells, namely,

$$Ag \mid AgCl, LiCl(a_1) \mid Li(Hg)_x$$

and
$$Li(Hg)_x \mid LiCl(a_2), AgCl \mid Ag.$$
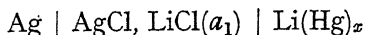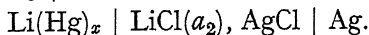
The e.m.f. (E) of the cell will be equal to the sum of the electromotive forces of the two simple cells ; that is, $E=\dfrac{2RT}{F} \log_e\dfrac{a_1}{a_2}$. If, therefore, one determines the e.m.f. of the concentration cell with transport and the e.m.f. of the concentration cell without transport, the transport number of the cation can be calculated from the relation[3]

$$n_c=\frac{u_c}{u_c+u_a}=\frac{E_t}{E}.$$

[1] Livingston and Lingane, *J. Chem. Educ.*, 1938, **15**, 320.
[2] Taylor and Perrott, *J. Amer. Chem. Soc.*, 1921, **43**, 484.
[3] See MacInnes and Beattie, *J. Amer. Chem. Soc.*, 1920, **42**, 1117, 1128.

EXPERIMENT.—*Determine the transport number of Lithium Ion in Lithium Chloride.*

The e.m.f. of cells arranged as described above, should be determined, in which the activities (concentrations) of lithium chloride are $a_1 : a_2 = 1\cdot0 : 0\cdot1$ and $a_1 : a_2 = 0\cdot3 : 0\cdot03$. At 25° the value of $n_c = 0\cdot304$ and $0\cdot317$ respectively.

Similarly, one may determine the transport number of chloride ion in hydrochloric acid by measuring the e.m.f. of the cells.

$$\text{H}_2 \mid \text{HCl}(a_1) \mid \text{HCl}(a_2) \mid \text{H}_2$$

and $$\text{H}_2 \mid \text{HCl}(a_1), \text{AgCl} \mid \text{Ag} \mid \text{AgCl}, \text{HCl}(a_2) \mid \text{H}_2$$
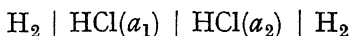
Determination of Hydrogen Ion Concentration by means of Indicators.—A substance used as an indicator is, generally, a weak acid of which the anion has a different colour from the un-ionized molecule. Thus, phenolphthalein is colourless in the un-ionized state (in acid solution), but red (colour of the anion) in the ionized state (in alkaline solution). In some cases, *e.g.* methyl orange, the indicator is coloured both in the un-ionized and in the ionized state, so that the passage from the acid to the alkaline state is accompanied by a change of colour.

The behaviour and use of indicators will be understood if one plots the dissociation curve of the indicator, regarded as a weak acid ; that is, if one plots the hydrogen ion concentration (or the pH value) against the degree of ionization of the indicator acid. The dissociation curve of a weak acid can be calculated by means of the equation

$$p\text{H} = \log_{10}\frac{1}{[\text{H}^{\cdot}]} = \log_{10}\frac{1}{K} + \log_{10}\frac{a}{1-a}$$

which is derived from the mass law equation, $\dfrac{[\text{H}^{\cdot}] \times [\text{A}']}{[\text{HA}]} = K$,

where K is the ionization constant or affinity constant. The curve for p-nitrophenol is shown in Fig. 101. In the case of p-nitrophenol, $K = 6\cdot5 \times 10^{-8}$, and $\log_{10}\dfrac{1}{K} = 7\cdot19$. From the above equation it follows that when $a = 0\cdot5$, $\log_{10}\dfrac{1}{[\text{H}^{\cdot}]} = p\text{H} = \log_{10}\dfrac{1}{K}$. If it be assumed that the depth of colour, as compared with the completely ionized indicator, is proportional to the degree of ionization, a, then the pH

value of the solution in which the colour of an indicator is midway between that of the completely un-ionized and completely ionized indicator ($\alpha=0.5$), will be equal to $\log_{10}\frac{1}{K}$, where K is the affinity constant of the (acid) indicator.

From the above equation it follows that the dissociation curves of the different indicators must have the same form, but will occupy different positions on the pH axis owing to the fact that K has different values in the case of different indicators. Consequently, the different indicators show a change in colour over different ranges of hydrogen ion concentration; and it is on this fact that the use of indicators for the determination of the pH value of a solution depends.

To illustrate this point, 10 ml. of each of the buffer solutions mentioned on p. 222 are placed in a series of dry test-tubes, and 3-5 drops of standard methyl orange indicator solution added to each. Note and tabulate the colour obtained in each case, and the pH value at which a colour change takes place. Repeat the same test with the indicators given in the following table.
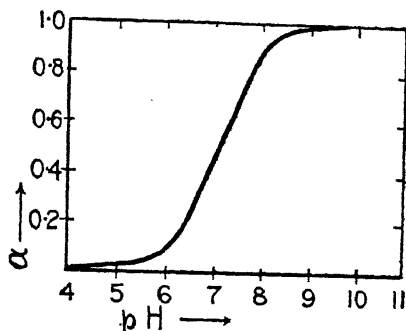
FIG. 101.

Indicator.	Ml. of N/20-NaOH to 1 g. of solid.	Concentration of indicator per cent.	pH range.
Thymol blue . . .	4·3	0·04	1·2–2·8
Bromphenol blue .	3·0	0·04	3·0–4·6
Bromcresol green .	3·1	0·04	3·8–5·4
Bromcresol purple .	3·7	0·04	5·2–6·8
Bromthymol blue .	3·2	0·04	6·0–7·6
Phenol red . . .	5·7	0·02	6·8–8·4
Cresol red . . .	5·3	0·02	7·2–8·8
Thymol blue . .	4·3	0·04	8·0–9·6

A knowledge of the pH value at which an indicator changes colour is of importance in deciding what indicator

may be used in acid-alkali titrations. An indicator can be used satisfactorily only when the pH value at which it changes colour lies on the steep portion of the titration curve (p. 236). Since the titration curve of a weak acid and weak alkali shows no such steep portion, no indicator will show a satisfactory end-point.

In using the indicator method of determining the pH value of a solution, it is necessary to have at one's command a series of indicators, the K values of which are distributed over the whole range of pH values to be investigated, and which give definite colour changes for particular concentrations (activities) of hydrogen ion. In the table (p. 245) is given a list of indicators recommended by Clark and Lubs and now generally used.[1]

In carrying out a pH determination colorimetrically, one may proceed as follows : To 10 ml. of the liquid under test add 5 drops of a mixed indicator (universal indicator) in order to obtain an approximate pH value. Suppose this value is in the neighbourhood of 8. From the preceding table one finds that this lies within the range of cresol red. One therefore adds to 10 ml. of the liquid under investigation, 5 drops of cresol red indicator solution, and the colour tint obtained is compared with the tints shown when cresol red is added to a series of buffer solutions having pH values lying between 7 and 9. The test liquid will have the same pH value as the buffer solution which gives the same colour tint with the same indicator, and since the pH value of the buffer solution is known from potentiometric measurements, the pH value of the test liquid is thereby ascertained.

Instead of using buffer solutions to which indicator has been added for the purposes of comparison, one may now obtain tinted glasses to represent the colour tints given by different indicators with solutions of known pH value.

To facilitate the matching of the unknown solution with the standards, the solution is placed in a stand (comparator) between two standards, the pH values of which differ only

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[1] Aqueous solutions of these indicators are prepared by grinding 0·1 gram of the dry compound with the amount of $N/20$-NaOH required to form the sodium salt. The solution obtained is diluted with water to 25 ml., thus giving a 0·4 per cent. solution. For use this is diluted further so as to give 0·04 or 0·02 per cent. solution. 5 drops of the indicator solution are added to 10 ml. of solution to be tested.

by 0·2, the solutions being viewed against a white background.

Hydrolysis of Salts.—The degree of hydrolysis of a salt may be obtained by determining the pH value of a salt solution colorimetrically. To 10 ml. of a solution of potassium cyanide add 3–5 drops of cresol red indicator solution, and compare the colour obtained with that given with a series of buffer solutions to which the same indicator has been added. Calculate K_h and compare the value with that calculated from the expression $K_h = K_w/K_a$. (K_a for hydrocyanic acid $= 1·3 \times 10^{-9}$.)

Decomposition Potential of Salts.—When a dilute solution of zinc sulphate is electrolysed between platinum electrodes, zinc is deposited on the cathode and oxygen is liberated at the anode. A cell of the type $Zn \mid$ solution $\mid O_2$ is thus obtained, and this cell exhibits a certain e.m.f. due to the tendency of the zinc and oxygen to pass back into the ionic state. The e.m.f. of the cell acts in the opposite direction to that of the electrolysing current. In order, therefore, that continuous electrolysis may take place, an e.m.f. must be applied to the electrodes sufficient to overcome the back e.m.f. of the products of electrolysis, and the potential which is just sufficient to produce continuous electrolysis is called the *decomposition potential* of the salt. It will obviously be equal to the sum of the electrode potentials plus the bath potential, or the potential fall between the electrodes, which is given by the expression $I \times R$, where I is the current passing, and R the resistance of the electrolyte between the electrodes.

Since the electrode potential, as we have already seen, depends on the concentration of the ions in the solution, so also the decomposition potential will depend on the concentration.

The decomposition potential of a salt can be most simply determined by measuring the current which passes when an e.m.f. of gradually increasing strength is applied to the electrodes. At first, an almost constant and very small current, the *residual current*, is obtained, but after the applied e.m.f. reaches a certain value, the current begins rapidly to increase with increase in the applied e.m.f. The point where this rapid increase in the electrolysing current commences, is the *decomposition potential* of the particular solution. If one plots the current strength against the

applied e.m.f. a curve such as is shown in Fig. 102 is obtained. When the break in the curve is not sharp, the value of the decomposition potential is obtained by producing the almost horizontal branch to cut the extension of the almost vertical branch.
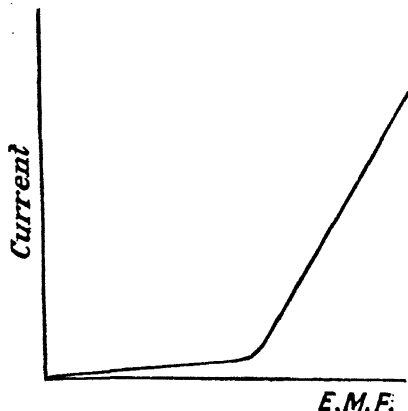

FIG. 102.

It is frequently also desired to obtain the value of the discharge potential of the anion and cation separately. This can readily be effected with the help of an auxiliary electrode, as described below.

EXPERIMENT. —*Determine the Decomposition Potential of a Solution of Zinc Sulphate.*

The apparatus is fitted up as shown diagrammatically in Fig. 103. Two lead accumulators are closed through the resistance R furnished with a sliding contact. A is a milliammeter, furnished with a shunt enabling readings to be taken up to 0·2 or 0·3 ampere. C is the electrolytic cell (a beaker) in which two platinum electrodes are placed. V is a high resistance voltmeter. A solution of 0·1N zinc sulphate may be employed.
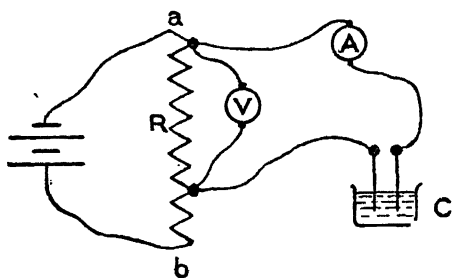
FIG. 103.

The sliding contact is first placed near the end *a* of the resistance so that only a small e.m.f. is applied to the electrodes of the electrolytic cell, and the current passing is read on the milliammeter. The applied e.m.f. is read on the voltmeter V. The sliding contact is then moved in steps towards the end *b* of the resistance, and at each point the current passing is read on A, and the applied e.m.f. on V. These corresponding values are plotted as shown in

Fig. 102, and the value of the decomposition potential read from the curve.

The correction for the fall of potential in the cell may also be applied.

FURTHER EXPERIMENTS.—*Determine the Decomposition Potential of Copper Sulphate (in Deci-normal Solution), of Silver Nitrate (Deci-normal), and of Potassium Silver Cyanide (Silver Nitrate with Excess of Potassium Cyanide).*

EXPERIMENT.—*Determine the Discharge Potential of Zinc Ion and Sulphate Ion in a Solution of Zinc Sulphate.*

The apparatus is fitted up as shown in Fig. 104. The circuit with resistance and ammeter is as in the previous experiment. E_1 and E_2 are two standard electrodes, $Hg \mid Hg_2SO_4$ in x-$H_2SO_4 \mid$, the side tubes of which are placed in the solution of zinc sulphate, quite close to the cathode and anode.

By means of the sliding contact, different potentials are applied to the elec-

FIG. 104.

trodes of the cell C, and the current is read on the ammeter A. At the same time one determines the e.m.f. of the combinations—

Standard Electrode | solution | Cathode of Cell
   a   *b*

Standard Electrode | solution | Anode of Cell
   a'   *b'*

by means of the ordinary compensation method (p. 199).

By subtracting from the values so found the potential of the standard electrode, one obtains the potential of the cathode and anode respectively. The values so obtained for different values of applied e.m.f. are plotted against the current, and one obtains two curves, one for the cathode and one for the anode, similar to that shown in Fig. 102.
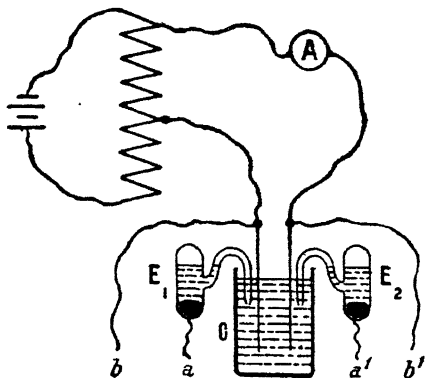
The break in the curve corresponds to the discharge potential of the cation and anion, and by adding these values the decomposition potential of the salt is obtained.

The potential of the standard mercurous sulphate electrode used above is +0·956 volt, the mercury being positive to the solution.

EXPERIMENT.—*Determine the Decomposition Potential of Hydrochloric Acid.*

Make up solutions of hydrochloric acid of concentration 2-N, N/2, N/8, N/32, N/64 and determine the decomposition potential, using platinum electrodes. Notice increase in decomposition potential as the concentration decreases. When the decomposition potential increases above the value 1·7 volts, oxygen as well as chlorine is evolved at the anode. (Why ?) In the more concentrated solutions, the residual current is comparatively large owing to the solubility of chlorine and to its diffusion to the cathode, where it recombines with hydrogen.

The decomposition potential of normal solutions of hydrobromic and of hydriodic acids may similarly be determined. For this purpose use N-HCl solution and add KBr or KI in amount equivalent to the HCl present.

Overvoltage.—When platinized platinum electrodes are partially surrounded by hydrogen and oxygen respectively, and dip in a normal solution of sulphuric acid, the e.m.f. of the cell is about 1·11 volt. When, however, a normal solution of sulphuric acid is electrolysed, the decomposition potential is greater than this value, and varies with the metal used as electrodes. For each metal a certain " excess voltage " is required in order that hydrogen or oxygen may be evolved as a gas.

EXPERIMENT.—*Determine the Decomposition Potential of Sulphuric Acid.*

Prepare an approximately normal solution of sulphuric acid and determine the decomposition potential, using electrodes of (1) platinized platinum, (2) polished platinum, (3) copper, (4) lead. The cathode potential should also be determined separately, using a normal mercurous sulphate electrode (p. 249).

CHAPTER XIII

VELOCITY OF CHEMICAL REACTION IN HOMOGENEOUS SYSTEMS

THE fact that all chemical reactions require time for their accomplishment gives rise to the problems : What are the laws governing the velocity of a chemical reaction, and how can the rate of change be measured ?

As regards the laws by which the velocity of a chemical reaction is governed, the basis of these is to be found in Guldberg and Waage's law of mass action. According to this law, the velocity with which a reaction occurs is, at any moment, proportional to the existing concentrations of the reacting substances. If reactions which are reversible to an appreciable extent are neglected and only those reactions are considered which take place practically completely in one direction, the velocity of reaction can be expressed by the equation—

$$\frac{dx}{dt} = k(a-x)(b-x)(c-x) \ . \ . \ .$$

where x represents the amount, in gram molecules, of the substances changed in time t, dx/dt the velocity of the reaction at any given moment, and a, b, c . . . represent the initial concentrations (in gram molecules per litre) of the interacting substances.

In the cases where only one molecular species undergoes change (unimolecular reaction or reaction of the first order), the velocity of the reaction will be represented by the equation $dx/dt = k(a-x)$; from which, on integration, one obtains the expression—

$$k = \frac{1}{t} \cdot \log_e \frac{a}{a-x} = 2 \cdot 303 \times \frac{\log_{10} a - \log_{10}(a-x)}{t}$$

When two molecular species undergo change in concentration during the reaction (bimolecular reaction or reaction

of the second order) the velocity of the reaction will be expressed by the equation $dx/dt = k(a-x)(b-x)$, which, on integration, yields the expression—

$$k = \frac{1}{(a-b)t} \cdot \log_e \frac{(a-x)b}{(b-x)a} = \frac{2\cdot303}{(a-b)t} \cdot \log_{10} \frac{(a-x)b}{(b-x)a}$$

When the initial concentrations, a and b, are the same, the corresponding equations are $\frac{dx}{dt} = k(a-x)^2$ and $k = \frac{1}{t} \cdot \frac{x}{a(a-x)}$.

The expressions for the velocity of reactions of a higher order, in which the concentration of three or more molecular species undergoes change, can be obtained in a similar manner. Such reactions are, however, few in number and will not be considered here.

It may be noted that when the concentration of one of the reactants in a bimolecular reaction is very much greater than that of the other, the concentration of the former will not appreciably alter during the process of change. The reaction will therefore be pseudo-unimolecular and will take place in accordance with the equation for a unimolecular change.

In order to follow the progress of a chemical reaction, use can be made of the ordinary methods of chemical analysis; or physical methods may be employed in those cases where the reaction is accompanied by a sufficiently definite or great change in the physical properties of the system. The actual method employed in any given case will depend, of course, on the reaction which is being studied, and one will naturally choose that method which can be carried out most conveniently and quickly, and at the same time with sufficient accuracy. In general, it is better to employ a physical method, where possible, on account of the fact that there is less danger, or no danger, of disturbing the condition of the reacting system; a danger which is by no means absent when a chemical method, depending as it must on the addition of other substances to the reacting system, is employed.

Of the physical methods which have received application for this purpose, one may mention : measurement of the change in volume of the system, and the change of the rotatory power, in the case of optically active substances. To these may be added, determination of the volume of gas evolved or absorbed during the reaction.

Of the chemical methods, one may employ those either of volumetric or of gravimetric analysis ; the former being employed, where possible, on account of the convenience and rapidity with which they can be carried out. In the case of reactions which proceed with considerable velocity, it may be necessary, when chemical methods of analysis are employed, to adopt means for stopping the reaction at a particular moment, or for so greatly reducing the velocity that practically no change occurs during the time necessary for carrying out the analysis.

A.—Unimolecular and Pseudo-unimolecular Reactions

There are comparatively few reactions (apart from gaseous reactions) which are truly unimolecular, but there are a large number which are pseudo-unimolecular.[1]   The reactions to be studied here are of this type.

Hydrolysis of an Ester in presence of an Acid.—When an ester, such as methyl acetate, is acted on by water, it is partially converted into alcohol and acid, according to the equation—

$$CH_3.COOCH_3 + H_2O \leftrightarrows CH_3.COOH + CH_3OH$$
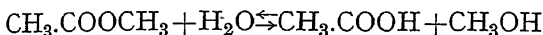
and when the amount of water is relatively large, the reaction takes place practically completely, as represented, from left to right (pseudo-unimolecular reaction).   This decomposition or hydrolysis of an ester, which takes place more or less rapidly even with pure water, is accelerated by the presence of acids ; and the acceleration is, in dilute solutions, proportional to the concentration of hydrogen ion. It is evident, therefore, that determinations of the velocity of hydrolysis of esters under the influence of acids, may be used for the purpose of determining the concentration of hydrogen ion in a solution.

The following experiments will illustrate this :—

EXPERIMENT.—*Determine the Relative Strengths of Hydrochloric and Sulphuric Acid.*

A standard solution of baryta, approximately N/20, should be prepared (p. 153), and its titre determined by means of pure succinic acid, using phenolphthalein as indi-

[1] See Moelwyn-Hughes, *Kinetics of Reaction in Solution.* (Oxford University Press.)

cator. By means of this baryta solution, prepare also semi-normal solutions of hydrochloric acid and sulphuric acid, the solutions being in all cases made up with CO_2-free water (p. 153). Procure also two small Erlenmeyer flasks of about 100 ml. capacity, preferably made of Jena or pyrex glass. These should be washed clean, then subjected to the action of steam for 10–15 minutes (p. 161), and thereafter dried; and they should also be fitted with corks, previously soaked in melted paraffin, and be weighted by means of leaden plates. The latter may be attached to the flasks either by turning up the edges of the lead round the flask, or by means of thin copper wire passing through the corners of the lead plate and twisted round the neck of the flask; or a band
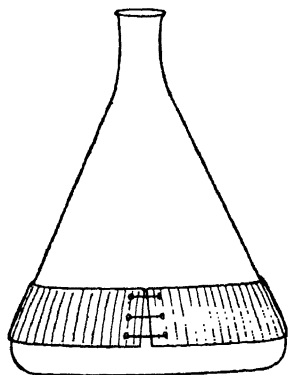
FIG. 105.

of lead may be made to encircle the lower portion of the flask (Fig. 105).

Into the two Erlenmeyer flasks, prepared as described above, pipette 40 ml. of the $0.5N$-HCl and $0.5N$-H_2SO_4 respectively, and place them in a thermostat, the temperature of which has been adjusted to $25.0°$ (p. 31). The flasks may be either suspended from the side of the thermostat or placed on a tray of strong wire-netting or perforated zinc plate, which should be placed at such a depth that the flasks are immersed up to the neck in the water of the thermostat. A stoppered bottle containing methyl acetate should also be placed in the thermostat.

After, say, ten minutes, when the liquids will have assumed the temperature of the bath, pipette 2 ml. of methyl acetate into one of the flasks of acid, shake well, and immediately withdraw 2 ml. of the solution. This is allowed to run into 20–30 ml. of CO_2-free water,[1] contained in a suitable Erlenmeyer flask, in order to arrest the reaction, and the acid titrated as soon as possible by means of the baryta solution. Note the moment, to the nearest second, at which the solution is run into the water; this is taken as the starting-point of the reaction.

[1] In order to arrest the reaction still more effectually, the water may be cooled by placing the flask in a basin of ice. This is, however, not absolutely necessary unless the titration with baryta is delayed unduly.

Having thus determined the initial titre of the one acid solution, 2 ml. of methyl acetate are pipetted into the second acid, and the initial titre determined as in the previous case.

About 10–15 minutes after the first titration, again withdraw 2 ml. of the mixture from each of the flasks, and determine the titre as before, noting, in each case, the moment at which the reaction is arrested. Further titrations are made from time to time in the same manner after successive intervals of, say, 20, 30, 40, 60, 120 minutes. The remainder of the reaction-mixtures should then be left in the thermostat for 48 hours, when the final titration may be made.

The value of the velocity coefficient, k, in the two cases can then be calculated in accordance with the formula for a unimolecular reaction (p. 251). Since the initial concentration a is proportional to $T_\infty - T_0$, where T_∞ is the final titration, and T_0 the initial titration in millilitres of the baryta solution ; and since $a - x$, the concentration at time t_n (counted in minutes from the commencement of the reaction) is proportional to $T_\infty - T_n$, where T_n is the titration at time t_n, one can write—

$$k = \frac{2 \cdot 303}{t_n} \left[\log_{10} (T_\infty - T_0) - \log_{10} (T_\infty - T_n) \right]$$

Instead of counting the time and the change of concentration from the beginning of the reaction, one can also reckon them from titration to titration. If T_x and T_y are the titrations at the times t_x and t_y, the velocity coefficient is given by the expression—

$$k = \frac{2 \cdot 303}{t_y - t_x} \left[\log_{10} (T_\infty - T_x) - \log_{10} (T_\infty - T_y) \right]$$

The results should be tabulated under the headings, *time, titration, k* ; the numbers in the first column giving the time in minutes from the commencement of the reaction at which the particular titration was made. The values of the velocity coefficient, calculated in accordance with the above expressions should not differ from the mean of all the values, in any given series, by more than 3–4 per cent. The first value, however, generally shows greater divergence, and may be excluded.

More accurate Method of Calculation.—Owing to the weight given to the end value, the accuracy of which is often less than that of the other individual determinations, the error in the value of k, calculated by means of the formulæ given above, frequently amounts to 2–4 per cent. The following procedure, which allows k to be computed with an accuracy of 0·2 to 0·5 per cent., should therefore be employed.[1]

A series of " readings," V (titrations, value of a physical property, etc.), is made at times $t_1 \ldots t_n$ spread over an interval two or three times the length of the period of half completion of the reaction. A second series of " readings," V', is then made at times $(t_1+t') \ldots (t_n+t')$, each exactly a constant interval t' after the corresponding " reading " V. The interval t' should be equal to 2–3 times the period of half-reaction. If the values of $\log_{10} (V'-V)$ are then plotted as ordinates against the times t as abscissæ, a straight line is obtained, the slope of which, $\log_{10}(V'-V)/t$, is $-k \cdot \log_{10}e$; or, $2\cdot303 \times \text{Slope} = -k$. (The slope of the straight line is negative.)

The value of the velocity coefficient in the case of the mixture 40 ml. 0·5N-HCl+2 ml. methyl acetate at 25° is 0·0032. From the known values of the " degree of ionization " of the acids (for 0·5N-HCl, $a=0\cdot85$; for 0·5N-H_2SO_4, $a=0\cdot53$), determine in how far your measurements indicate proportionality between the value of the velocity coefficient and the concentration of hydrogen ion in the solutions as calculated from conductivity measurements; and conversely, assuming direct proportionality to exist, calculate from your values of the velocity constants the " degree of ionization " of hydrochloric and sulphuric acids in semi-normal solution (*see below*).

It will also be found very instructive (see p. 267) to carry out another measurement with the same amount of, say, hydrochloric acid as used above, but with double the quantity (4 ml.) of methyl acetate. This experiment should, ndeed, be carried out alongside of those just described.

EXERCISE.—From the measurements made above, plot the values of x (the amount of reacting substance changed), against the corresponding values of the time, in rectangular co-ordinates. Draw a

[1] Guggenheim, *Phil. Mag.*, 1926, [vii], **2**, 538. See also Roseveare, *J. Amer. Chem. Soc.*, 1931, **53**, 1651; Reed and Theriault, *J. Phys. Chem.*,

smooth curve through the points so obtained, and from the portion of the curve at which concordance with the observed values is best, calculate the value of the velocity constant. From the form of the curve, also, determine the influence of titration and time errors at different stages of the reaction.

Integration of the equation, $dx/(a-x) = k.dt$, gives the expression: $\log_e(a-x) = k.t + \text{constant}$, or $\log_{10}(a-x) = (k/2.303).t + \text{constant}$. Plot the values of $\log_{10}(a-x)$, or of $\log_{10}(T_\infty - T_x)$, obtained from the above determinations, against the time, t, and draw the best straight line through the experimental points. Multiply the slope of the curve (*i.e.* $\Delta.\log(a-x)/\Delta.t$) by 2.303, and so obtain the value of k.

While the proportionality between hydrogen ion concentration, as measured by ac (where c = concentration of acid), holds in the case of weak acids, the proportionality is no longer strictly valid in the case of strong acids, since ac is no true measure of ionic concentration. Moreover, the phenomenon known as "neutral salt action" (p. 230) is met with. Determinations of the velocity of hydrolysis of methyl acetate in $0.5N\text{-HCl}$, to which varying amounts of potassium chloride are added, may be carried out.[1]

Temperature Coefficient of Reaction Velocity.—The velocity with which a chemical reaction takes place is generally greatly increased by rise of temperature. The ratio of the velocity coefficients at two temperatures different by 10°, *e.g.* $\dfrac{k_{35°}}{k_{25°}}$, is known as the temperature coefficient of the reaction, and very commonly has a value between 2 and 3. In recent years, much attention has been paid to the study of temperature coefficients for the purpose of gaining an insight into the mechanism of chemical change. From this study the theory of molecular activation arose,[2] according to which only a certain number of the molecules undergoing change are active; and the increase of reaction velocity with temperature is explained as due to a rapid increase in the number of active molecules.

Experiment has shown that the variation of the velocity coefficient, k, with temperature can be expressed by the equation, due to Arrhenius, $\dfrac{d \log_e k}{dT} = \dfrac{E}{RT^2}$, where E is interpreted as the critical increment or the energy of activation;

[1] See Brönsted and Teeter, *J. Physical Chem.*, 1924, **28**, 579; Brönsted and King, *J. Amer. Chem. Soc.*, 1925, **47**, 2523; Harned and Hawkins, *ibid.*, 1928, **50**, 85; Robinson, *T. Faraday Soc.*, 1930, **26**, 217.

[2] Arrhenius, *Z. physikal. Chem.*, 1889, **4**, 226.

that is, the energy required to activate a gram-molecule of substance. Assuming that E is independent of the temperature, the above equation yields, on integration, the expression : $\log_e \dfrac{k_2}{k_1} = \dfrac{E}{R}\left(\dfrac{1}{T_1} - \dfrac{1}{T_2}\right)$, where k_1 and k_2 are the velocity coefficients at the absolute temperatures T_1 and T_2, and R is the gas constant in heat units, 1·99 cal. per degree. Hence,

$$E = \frac{2 \cdot 303 \, \log_{10}\dfrac{k_2}{k_1} \times R \times T_1 \times T_2}{T_2 - T_1}$$

EXPERIMENT.—*Determine the Temperature Coefficient of the Hydrolysis of Methyl Acetate and Calculate the Critical Increment.*

The velocity of hydrolysis of methyl acetate in presence of 0·5N-HCl is determined at 35°, in the manner described on p. 254, and the velocity coefficient calculated therefrom. From the value so obtained and the value obtained at 25°, calculate the temperature coefficient of the reaction and the heat of activation or critical increment E.

Velocity of Inversion of Cane Sugar.—Another pseudo-unimolecular reaction is the inversion of cane sugar in dilute solution, the velocity of which is also accelerated by acids to a degree which is approximately proportional to the concentration of the hydrogen ion. Consequently, this reaction can also be employed for the determination of the concentration of hydrogen ion in a solution.

In order to follow the course of the reaction, use is made of the property of the solution of rotating the plane of polarized light. Whereas cane sugar is dextro-rotatory, invert sugar (mixture of glucose and fructose) is lævo-rotatory, so that, as the result of the inversion, the sign of rotation changes from right to left.

If A_0 represents the initial angle, and A_∞ the final angle of rotation, after complete inversion has occurred, the initial amount of cane sugar will be proportional to the total change in rotation, *i.e.* to $A_0 - A_\infty$. Similarly, at time t_n, if the angle of rotation is A_n, the amount of cane sugar present will be represented by $A_n - A_\infty$. Hence, in accordance with the formula for a unimolecular reaction, one obtains the expression—

$$k = \frac{2 \cdot 303}{t_n}\left[\log_{10}(A_0 - A_\infty) - \log_{10}(A_n - A_\infty)\right]$$

or, if the coefficient is calculated from reading to reading—

$$k=\frac{2\cdot303}{t_y-t_x} [\log_{10} (A_x-A\infty)-\log_{10} (A_y-A\infty)]$$

In carrying out the calculation, the values of the angles must be given their proper sign, rotations to the right being reckoned $+$, and those to the left $-$.

EXPERIMENT.—*Determine the Velocity Coefficient of Inversion of Cane Sugar by Semi-normal Hydrochloric Acid.*

Before commencing this experiment, read through the section on polarimetric measurements, p. 118.

Prepare a solution of cane sugar by dissolving 20 g. of pure cane sugar in water and making the volume up to 100 ml.; and, if necessary, filter the solution so that it is quite clear. Add a small crystal of mercuric iodide as preservative. Prepare, also, a normal solution of hydrochloric acid. Place 25 ml. of the sugar solution and about 30 ml. of the acid in separate flasks which have previously been steamed out and dried (p. 161), and stand them in a thermostat at 25°.

After having set up the polarimeter and determined the zero,[1] place a jacketed observation tube in the polarimeter, and cause water (at 25°) to circulate through the mantle of the observation tube (p. 42). The circulation of water through the tube must be so regulated that the temperature remains constant to within 0·1° during the whole of the experiment. This should first be tested with the observation tube full of water, in which the bulb of a thermometer is immersed.

The circulation of the water having been satisfactorily regulated, the observation tube is dried and replaced in the polarimeter. When the temperature has again become constant, add 25 ml. of the acid to the sugar solution, and, as soon as possible, pour the mixture into the observation tube. Determine the angle of rotation, and note the time at which the reading is made. Preserve a quantity of the mixed sugar and acid solution in a stoppered flask in the thermostat, for the final reading of the rotation.

As the angle of rotation alters rather quickly during the

[1] It will not be necessary to introduce the zero correction, because one is dealing here with differences of angles; but the zero point should, nevertheless, be determined before and after the experiment in order to make sure that it does not change during the progress of the experiment.

first few minutes, a series of five or six readings should be made, one after the other, and the time noted at which the first and last readings are made. The mean value of the angles read, and the middle point of the time period between the first and last readings, should be taken as the initial value of the rotation (A_0) and the starting-point of the reaction, respectively. Further readings, up to the number of eight or ten, of the angle of rotation should be made after periods gradually lengthening from ten minutes to two hours. The observation tube may then be cleaned out and the final rotation determined after at least 48 hours with the solution which had been kept in the thermostat.

The value of the velocity coefficient should be calculated according to one or other of the expressions given on p. 258, and the results tabulated under the headings *time, rotation, k.*

The velocity coefficient for a 20-per-cent. sugar solution, when mixed with an equal volume of normal hydrochloric acid at 25°, is 0·00472.

Similar measurements should be carried out with corresponding solutions of other acids, and the values of the constants so obtained compared.[1] Determine also the velocity coefficient at 35° and calculate the temperature coefficient and the critical increment.[2]

Application.—As the experiments just described will have shown, the measurement of the velocity of hydrolysis of an ester, or of the inversion of cane sugar in presence of acids, gives a means of determining the concentration of hydrogen ion in a solution ; and as an illustration of the application of such measurements for this purpose, one may determine the degree of hydrolysis of a salt of a weak base and strong acid (cf. p. 149).

When such a salt as carbamide hydrochloride is dissolved in water, partial hydrolysis takes place with formation of free (practically un-ionized) carbamide and hydrochloric acid. If the hydrochloric acid is regarded as being completely ionized, then it will be clear that the degree of hydrolysis of the salt will be measured by the concentration of free hydrogen ion produced in the solution. The reactions which have just been studied afford a means of determining this, all that is necessary being to determine, first of all, the velocity of hydrolysis of methyl acetate or the inversion of cane sugar in solutions containing a known concentration of hydrogen ion, and then in a solution of the salt of known concentration.

EXPERIMENT.—*Determine the Degree of Hydrolysis of Carbamide Hydrochloride.*

[1] See Worley, *J. Chem. Soc.*, 1911, **99**, 349 ; Moran and Lewis, *ibid.*, 1922, **121**, 1613 ; Taketomi, *J. Soc. Chem. Ind. Japan*, 1929, **32**, 260B.
[2] Lamble and Lewis, *J. Chem. Soc.*, 1915, **107**, 233.

Determine, in the manner described on p. 254, the velocity constant of hydrolysis of methyl acetate first of all in a semi-normal solution of hydrochloric acid, and then in a solution of semi-normal hydrochloric acid in which an amount of carbamide exactly equivalent to the amount of hydrogen chloride present in the solution, has been dissolved; the amount of methyl acetate added and the temperature of the experiment being the same in both cases. It is best, indeed, to carry on the two experiments side by side.

The degree of hydrolysis is given by the ratio of the concentration of free acid present in the solution to that which would be present if the salt were completely hydrolysed. The latter is, of course, measured by the velocity constant (k_1) in the pure acid solution, and the former by the velocity constant obtained after the addition of an equivalent amount of carbamide (k_2). Hence, $x = k_2/k_1$, where x is the degree of hydrolysis.

With the solutions given above, $k_1 = 0.0032$, and $k_2 = 0.00208$. Hence, in semi-normal solution at $25°$, the degree of hydrolysis of carbamide hydrochloride is 0.65; that is to say, 65 per cent. of the salt is hydrolysed.

More Accurate Method.—It has been assumed above that the velocity constant of hydrolysis of methyl acetate is proportional to the free *acid* present, but this is only approximately true. The concentration of hydrogen ion will not be equal to the total concentration of acid, owing to the presence of a salt of the acid; and, further, the velocity will also be affected by the presence of the neutral salt. These two factors can be corrected for in the following manner. A determination of the approximate degree of hydrolysis is carried out as described above, by which the degree of hydrolysis is found to be apparently 65 per cent. A solution of hydrochloric acid and sodium chloride is then prepared so that it is semi-normal with respect to total chloride, but contains only 65 per cent. of this as free acid. The velocity constant obtained with this solution is then compared with the constant obtained with the solution of carbamide hydrochloride.[1]

The degree of hydrolysis can also be obtained by studying the velocity of inversion of cane sugar. The procedure to be adopted in this case will be quite clear from what has just been said, and from the description of the experiment on p. 258.

These two methods of determining the degree of hydrolysis can be used in the case of other salts formed from a weak base and a strong acid, provided the base is very weak. In the case of salts of bases of the strength, say, of aniline, the method is not suitable (cf. p. 149).

Decomposition of Diazonium Salts.—In illustration of another method of following the course of a reaction, one may study the decomposition of diazonium salts, *e.g.* benzene diazonium chloride.[2] When this salt is warmed with excess

[1] Walker and Wood, *J. Chem. Soc.*, 1903, **83**, 484.
[2] Cain and Nicoll, *J. Chem. Soc.*, 1902, **81**, 1412; 1903, **83**, 206, 470. ⸳ ⸳ *T. Faraday Soc.*, 1940. **36**, 948.

of water, it undergoes decomposition according to the equation—

$$C_6H_5.N_2.Cl + H_2O = C_6H_5OH + HCl + N_2$$
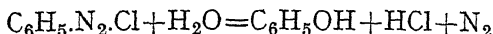
and the course of the decomposition can be followed by measuring the volume of nitrogen evolved from time to time.

Since the concentration of benzene diazonium chloride in the solution is proportional to the total volume of nitrogen which the solution is capable of yielding, one can calculate the velocity coefficient of the decomposition by means of the formula—

$$k = \frac{2 \cdot 303}{t} \left[\log_{10} V_\infty - \log_{10} (V_\infty - V_n) \right]$$

where V_∞ is the total volume of gas obtained, and V_n the volume of gas collected up to time t_n.

EXPERIMENT.—*Determine the Velocity of Decomposition of Benzene Diazonium Chloride.*

Prepare a solution of benzene diazonium chloride as follows : Dissolve 6·64 g. of aniline in 21·4 ml. of hydrochloric acid (sp. gr.=1·16) ; cool in ice-water, and add gradually from a dropping-funnel a cold solution of 4·9 g. of sodium nitrite in 75 ml. of water. After the addition of the sodium nitrite, make the solution up to 1 litre. Place 30–35 ml. of this solution in a tube of about 3 cm. in diameter, into which a side tube, B, of about 1 mm. bore is sealed (Fig. 106). The tube, which should be well cleaned and dried before use, should be chosen of such a length that the air-space above the solution is small. The capillary side tube B is connected with a Hempel gas burette, or ordinary burette, exactly as shown in Fig. 23, p. 50. The mouth of the tube A is closed by a rubber stopper through which a stirrer, S, passes, and the latter is furnished with a mercury seal, M, to prevent the escape of gas.

The construction of such a mercury seal, which is of great value in physico-chemical work, will be readily understood from Fig. 107. Through the rubber stopper R there passes a tube, *a*, which is slightly wider than the stem of the stirrer S. Passing about half way through the rubber stopper is the moderately wide tube *b*, which forms a cup round the tube *a*. Attached by corks or rubber stoppers (rubber tubing) to the upper portion of the stem of the stirrer, are two tubes, *c* and *d*, the former of which is of the same diameter as *a*, while the latter has a width intermediate between that of *a* and *b*. It should be long enough to reach down nearly to

the bottom of the mercury cup formed by *b*. Mercury is poured into the tube *b* so as to rise to about 1 cm. above the lower end of *d*. In this way a joint is obtained which, while allowing the stirrer to be rotated, prevents escape of gas from the inside of the tube.[1] The upper end of the tube *a* and the lower end of *c* should be cut straight, and the ends rounded in a flame. To reduce the friction, the stem of the stirrer where it passes through the tube *a* should be well coated with vaseline.[2]

In place of the mercury seal described above, one may also use " Quickfit " stirrers [3] with air-tight glands.

The solution of benzene diazonium chloride having been
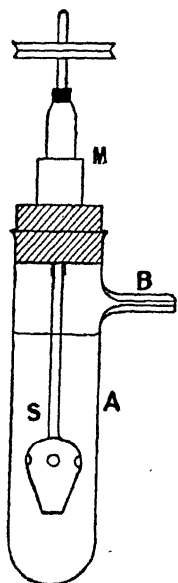
FIG. 106.
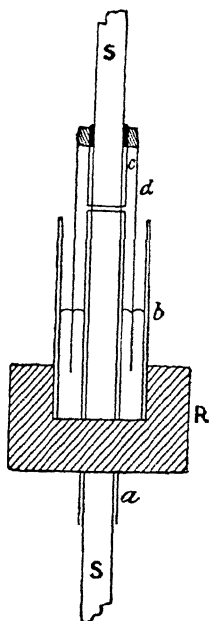
FIG. 107.

placed in the tube A (Fig. 106), the stirrer is inserted, and the apparatus then fitted together, the side tube B being connected with a gas burette, as shown in Fig. 23. The tube with the diazo-solution is immersed up to the level of the

[1] Provided, of course, the pressure is not allowed to become so great as to force air out through the mercury. Attention should be paid to this.

[2] Certain advantages are to be gained by replacing the tube *c* by a guide tube which is placed immediately below the driving pulley and on which the pulley rests (Howell, *Proc. Roy. Soc.*, 1923, A, **104**, 134).

[3] Made by Quickfit and Quartz, Ltd., London, for use with standard ground glass joints.

cork in a thermostat, the temperature of which is regulated at about 30°, and the stirrer is set in fairly rapid motion. During this time the tube with the solution should be in open communication with the air, and the gas evolved allowed to escape. After 5–7 minutes, communication with the gas burette is effected while that with the outside air is stopped, and the time at which this is done is noted. This is taken as the starting-point of the reaction. Gas will now collect in the burette, and its volume should be read off at intervals of about 30 minutes. The temperature of the gas and the height of the barometer should also be noted.

The end point of the reaction is determined by repeatedly immersing the tube with the reaction mixture in a large beaker of hot water, until, on cooling again to the temperature of the experiment, there is no further increase in the volume of gas evolved.

The velocity constant of the decomposition is then calculated by means of the equation given on p. 262, the results being tabulated under the headings, *time* ; *volume of* N_2 *in ml.* ; *temperature* ; *barometer* ; *corrected volume of* N_2 *in ml.* ; *k.*

Other unimolecular or pseudo-unimolecular reactions which may be studied are : decomposition of nitrosotriacetonamine in presence of alkali ; [1] decomposition of nitramide in acid solution ; [2] change of N-chloroacetanilide into *p*-chloroacetanilide in presence of hydrochloric acid ; [3] decomposition of nitrogen pentoxide into nitrogen tetroxide and oxygen in carbon tetrachloride solution. [4]

When a reaction is accompanied by a considerable change of volume, the progress of the reaction may be followed dilatometrically. Pseudo-unimolecular reactions which may be studied in this way are the hydrolysis, in acid solution, of ethyl orthoacetate and ethyl orthocarbonate. [5]

B.—REACTIONS OF THE SECOND ORDER

Saponification of Esters by Alkalis.—In aqueous solution in presence of alkali, esters undergo hydrolysis, or *saponification* ; and the velocity of saponification is approximately

[1] Francis and Clibbens, *J. Chem. Soc.*, 1912, **101**, 2358 ; Francis and Geake, *ibid.*, 1913, **103**, 1722.

[2] Brönsted and Pedersen, *Z. physikal. Chem.*, 1924, **108**, 185.

[3] Blanksma, *Rec. Trav. Pays. Bas.*, 1902, **21**, 366 ; 1903, **22**, 290.

[4] Eyring and Daniels, *J. Amer. Chem. Soc.*, 1930, **52**, 1472.

[5] See Brönsted and Wynne-Jones, *T. Faraday Soc.*, 1929, **25**, 59. See also Kilpatrick and Chase, *J. Amer. Chem. Soc.*, 1931, **53**, 1732.

proportional to the concentration of OH'. The reaction is represented by the equation—

$$CH_3.COO.C_2H_5 + OH' = CH_3.COO' + C_2H_5OH$$
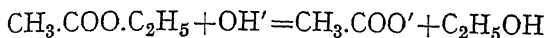
This reaction differs, as will be seen, from the hydrolysis of esters in presence of acid, by the fact that the concentration of the catalyst (OH') does not remain constant during the reaction, but gradually diminishes.

EXPERIMENT.—*Determine the Velocity of Saponification of Ethyl Acetate with Sodium Hydroxide.*

The measurement of the velocity of this reaction is carried out in a manner very similar to that used with methyl acetate and acid. As, however, hydrolysis takes place with very much greater velocity in presence of alkalis than in the presence of acids, the measurement is more difficult.

Place 50 ml. of M/60 solution of ethyl acetate in an Erlenmeyer flask (capable of holding about 100 ml.), which has previously been steamed out and dried. The flask is fitted with a paraffined cork and placed in a thermostat at 25°. Into another flask, similarly prepared, are introduced 50 ml. of N/30- or N/40-NaOH (free from carbonate, see p. 180). When these two solutions have acquired the temperature of the bath, the alkali is poured as rapidly as possible into the ester solution, and the mixture well shaken. The mean point of the time-interval required to add the alkali to the ester solution is taken as the initial point of the reaction ; and the alkali titre of the mixture corresponding with this moment is calculated from the known strength of the alkali solution, after subtracting the amount of alkali left in the flask. The latter should be determined by titration.

At intervals of 3, 5, and 10 minutes, and then after increasingly greater intervals, 10 ml. of the reaction mixture are withdrawn and allowed to run into a known volume of standard HCl (say N/20), contained in a small flask (or in several small flasks) fitted with a paraffined cork. The mean point of the interval required for the pipette to deliver is taken as the time of stopping the reaction. The excess of acid is titrated with baryta solution. After six or seven titrations have been made, the remainder of the reaction mixture is allowed to stand in the thermostat for twenty-four hours, and the final titration then made.

The velocity coefficient of saponification is then calculated

by means of the formula for a bimolecular reaction (p. 252), viz.—

$$k = \frac{2 \cdot 303}{T_\infty t} \left[\log_{10} T_t + \log_{10}(T_0 - T_\infty) - \log_{10} T_0 - \log_{10}(T_t - T_\infty) \right]$$

where T_0, T_t, T_∞ are the number of millilitres of acid solution required to neutralize the alkali in the reaction mixture, at the beginning of the reaction, at the time t minutes, and at the end of the reaction respectively. In order to reduce the values of the constant so obtained to those which would be obtained with normal solutions (containing 1 g.-equiv. per litre), the above expression must be multiplied by v/N, where v is the number of millilitres of the reaction mixture withdrawn each time for titration (in the above case 10 ml.), and N is the normality (concentration in gram-equivalents per litre) of the hydrochloric acid (in the above case 0·05).

The results should be tabulated under the headings *time* (in minutes) ; *number of ml. of HCl* ($N = x$) ; *k*.

For ethyl acetate and caustic soda at 25°, $k = 6 \cdot 94$. Deviations of 5 per cent. from the mean are allowable.

The course of the preceding reaction can also be followed by conductivity measurements. See Walker, *Proc. Roy. Soc.*, 1906, A, **78**, 157 ; Findlay and Hickmans, *J. Chem. Soc.*, 1909, **95**, 1003.

Additional Exercises.—Other suitable bimolecular reactions which may be studied are the following : Reaction between ethyl bromacetate and sodium thiosulphate (Slator, *J. Chem. Soc.*, 1905, **87**, 481) ; reaction between hydrogen peroxide and hydriodic acid in the presence of various catalysts (Brode, *Z. physikal. Chem.*, 1901, **37**, 257) ; reaction between potassium persulphate and hydriodic acid (Price, *Z. physikal. Chem.*, 1898, **27**, 477) ; velocity of esterification of acids by alcohols (Goldschmidt and Udby, *Z. physikal. Chem.*, 1907, **60**, 728 ; Lapworth and Partington, *J. Chem. Soc.*, 1910, **97**, 19).

Order of a Reaction.—In employing measurements of reaction velocity for the purpose of determining the mechanism of a chemical reaction, the first point which has to be settled is the order of the reaction. This is not always given by the number of reacting molecules as expressed in the ordinary chemical equation ; indeed, it is very seldom so given except in the case of the simplest reactions.

For the purpose of deciding this important point, various methods may be employed. One of the most important ·consists in making several measurements of the velocity of the reaction, starting with different concentrations of the reacting substances, and determining, in each case, the time required for a certain fraction (say, one-third or one-half)

of the total change to occur.   For a unimolecular reaction, the times are independent of the initial concentration ; for a bimolecular reaction, in which equimolecular quantities of the reactants are present initially, they are inversely proportional to the initial concentrations.

EXPERIMENT.—*Determine the Order of Reaction in the Case of the Hydrolysis of an Ester in Presence of Acid.*

For this purpose, two experiments should be carried out with methyl acetate and hydrochloric acid (see p. 254), using the same amount of acid in each case, but twice as much methyl acetate in one case as in the other.   The results should then be plotted in rectangular co-ordinates, the times of titration (in minutes) being plotted as ordinates, and the corresponding values of $a-x$ (or $T_\infty - T_n$) as abscissæ. From the curves obtained, the time should be read off corresponding to the abscissa $a-x=\frac{1}{2}a$ (or $T_\infty - T_n = \frac{1}{2}(T_\infty - T_0)$).   The time so found should be the same in the two cases.

A similar experiment may be carried out in the case of the saponification of an ester with alkali, or in the case of one of the bimolecular reactions referred to on p. 266.

It may be noted that in the case of a unimolecular reaction, $dx/(a-x)=k \cdot dt$.   That is, during any small unit of time, dt, the same fraction of the amount of substance present undergoes change.   If, therefore, the values of $(a-x)$ are plotted against time, one can read off from the curve, for successive equal short intervals of time (5–10 mins.), the value of dx and the mean value of $(a-x)$ during the particular interval of time.   If the successive values of $dx/(a-x)$ are constant, the reaction is unimolecular.

Catalysis.—In carrying out the experiments described in the preceding pages, it will have been found that the rate of a reaction, *e.g.* hydrolysis of methyl acetate, is markedly affected by the presence of a substance (acid) the amount of which undergoes no change during the reaction.   To this phenomenon, the term *catalysis* is given.   In preparative work, both in the laboratory and in industry, catalysis is of the highest importance and exhibits certain characteristics which may usefully be illustrated by experiment.   Of these characteristics, one of the most important is the magnitude of the effect produced relatively to the amount of catalyst producing it.   Further, the activity of a catalyst may sometimes be increased by the presence of another substance (known as a *promoter*) which may not itself be a catalyst

for the reaction ; and the activity of a catalyst may also be inhibited (" poisoned ") more or less completely by the presence of other substances, sometimes in quite minute traces. Several of these characteristics are found in the case of the reactions already described or referred to (*e.g.* reaction between potassium persulphate and hydriodic acid (p. 266), but are perhaps more easily studied in connection with the decomposition of hydrogen peroxide.

Hydrogen peroxide undergoes decomposition in accordance with the equation $H_2O_2 = H_2O + \frac{1}{2}O_2$, and the rate of decomposition is markedly accelerated by the presence of various catalysts. The course of the reaction may be followed either by titrating the hydrogen peroxide with potassium permanganate in acid solution, or by collecting the oxygen evolved (p. 262). The latter method is in many cases the more accurate.

The following experiments may be carried out.

1. *Decomposition of Hydrogen Peroxide with Colloidal Platinum as Catalyst.*[1]

An approximately 0·5 per cent. solution of hydrogen peroxide is prepared by diluting commercial 10-volume hydrogen peroxide (approximately 3 per cent. solution) to five or six times its volume with distilled water. To 25 ml. of this stock solution, contained in a small Erlenmeyer flask of pyrex or other resistant glass, 5 ml. of water are added, and after the solution has taken the temperature of the thermostat (say, 25°), 5 ml. are withdrawn, run into dilute sulphuric acid and titrated with 0·05N- (0·01M)-KMnO₄. Further titrations may be carried out at hourly or two-hourly intervals. This experiment enables one to determine the very slow, spontaneous decomposition of the hydrogen peroxide.

A series of experiments is now carried out successively by adding to 25 ml. of the stock solution of hydrogen peroxide 5 ml. of colloidal platinum sols, of different concentrations, the solutions being brought to the temperature of the thermostat before mixing. The time of mixing is noted and 5 ml. of the mixture are withdrawn at intervals, run into dilute sulphuric acid and titrated with permanganate. Plot the titrations against the time intervals from the moment of mixing.

[1] Bredig and Müller von Berneck, *Z. physikal. Chem.*, 1899, **31**, 258.

The colloidal platinum sol can be prepared as follows: 500 ml. of a platinum chloride solution (1 g. chloride in 1 litre of water), previously rendered slightly alkaline by addition of potassium carbonate, is heated to boiling. To this hot solution 2–4 ml. of a 33 per cent. solution of acrolein are added. A yellow colour appears which rapidly darkens to black. This black sol is filtered and, after addition of an equal volume of distilled water, is dialysed. The concentration of the sol can be determined by adding hydrochloric acid to a known volume, and filtering off and weighing the flocculated platinum.

The colloidal platinum sol may also be prepared by the Bredig method.[1] Thick platinum wires, pushed through glass tubes for convenience in handling, are connected with a source of electricity (50–100 volts). By lightly bringing together the ends of the platinum wires, immersed in ice-cold water, an arc is formed and the metal is dispersed in the form of a dark cloud. The arc lasts only for a moment and must be repeatedly re-formed. When sufficient metal has been dispersed, the colloidal sol is filtered. The concentration of the sol can be determined as indicated above. If necessary the sol may be concentrated by evaporation under reduced pressure. (The most concentrated platinum sol to be used may contain, say, about 0·2 g. of platinum per litre. From this, other sols can be prepared by dilution with water.)

2. *" Poisoning " the Catalyst.*[2]—The poisoning of a catalyst can be illustrated by the action of mercuric chloride on colloidal platinum.

In the manner described above, the rate of decomposition of hydrogen peroxide is determined after addition of platinum sols containing the same amount of platinum but varying amounts (0·005 g.-mol. $HgCl_2$ per litre and less) of mercuric chloride.

3. *Ferric Chloride as Catalyst.*[3]—To 25 ml. of the stock solution of hydrogen peroxide contained in a tube similar to that shown in Fig. 106 (p. 263) and fitted with a stirrer, 5 ml. of a solution of ferric chloride are added. This solution should contain, say, 0·05 gram-mol. of ferric chloride and 0·4 gram-mol. of hydrochloric acid per litre. The solutions should be allowed to attain the temperature of the thermostat before mixing. After mixing, the solution should be stirred and the volume of oxygen evolved read off from time to time (*cf.* Experiment, p. 262). From this

[1] *Z. angew. Chem.*, 1898, **41**, 951. The method has been modified by Svedberg, *Herstellung Kolloider Lösungen aanorgnischer Stoffe*.
[2] Bredig and Müller von Berneck, *Z. physikal. Chem.*, 1899, **31**, 324; Bredig and Ikeda, *ibid.*, 1901, **37**, 1.
Bohnson, *J. Phys. Chem.*, 1920, **24**, 677; Bohnson and Robertson, *J. Amer. Chem. Soc.*, 1923, **45**, 2493, 2512.

the rate of decomposition can be calculated.   The catalytic effect of solutions with a higher or lower concentration of ferric chloride, but the same concentration of acid, may be studied.

4. *Ferric Chloride as Catalyst promoted by Cupric Chloride.*[1] —The promoter action of cupric chloride may be studied by adding to 25 ml. of the hydrogen peroxide solution, 5 ml. of a solution containing 0·05 g.-mol. of ferric chloride, 0·4 g.-mol. of hydrochloric acid and varying amounts of cupric chloride (0·5 to 5·0 millimoles per litre).   With increasing concentration of cupric chloride, the promoter action increases to a maximum and then decreases.

[1] Bohnson and Robertson, *J. Amer. Chem. Soc.*, 1923, **45**, 2512.

CHAPTER XIV

THERMO-CHEMISTRY

WHEN a chemical reaction occurs, it is, in general, accompanied by a measurable heat effect—absorption or evolution of heat—and the amount of heat absorbed or evolved depends (1) on the nature of the reaction ; (2) on the condition (temperature and physical state) of the reacting substances ; (3) on the amounts of the substances. When, therefore, the last two factors remain the same, the heat effect accompanying a chemical reaction is a constant for that reaction.

In the case of the measurements to be considered in this chapter, the effect of temperature will not make itself felt. The physical state of the reacting substances, however, must be specified in each case, unless it is sufficiently obvious from the conditions of the experiment ; and the quantity of reacting substance must likewise be stated. As a rule, the heat effect of a reaction is referred to 1 gram equivalent or to 1 gram-molecule of the reacting substances, or of the substance produced.

The general method by which the heat of a reaction is measured, is to determine the elevation or depression of temperature produced in a known mass of a substance, generally water, of known specific heat. The heat of reaction is thus obtained as a product of specific heat, mass, and change of temperature.

Apparatus.—The essential part of the apparatus is the *calorimeter*, in which the reaction, the heat of which is to be measured, takes place. This is generally cylindrical in shape, and is usually made of silver, gilded internally ; or of nickel, copper, or aluminium.[1] It should have a capacity of upwards of 500 ml., in order to contain a sufficiently large amount of the reaction mixture and so help to minimize

[1] For many purposes a highly exhausted, silvered Dewar vacuum vessel forms a very suitable calorimeter.

errors due to radiation. To diminish the actual loss or gain of heat by radiation, the outer surface of the calorimeter is polished, and is surrounded by several other cylindrical
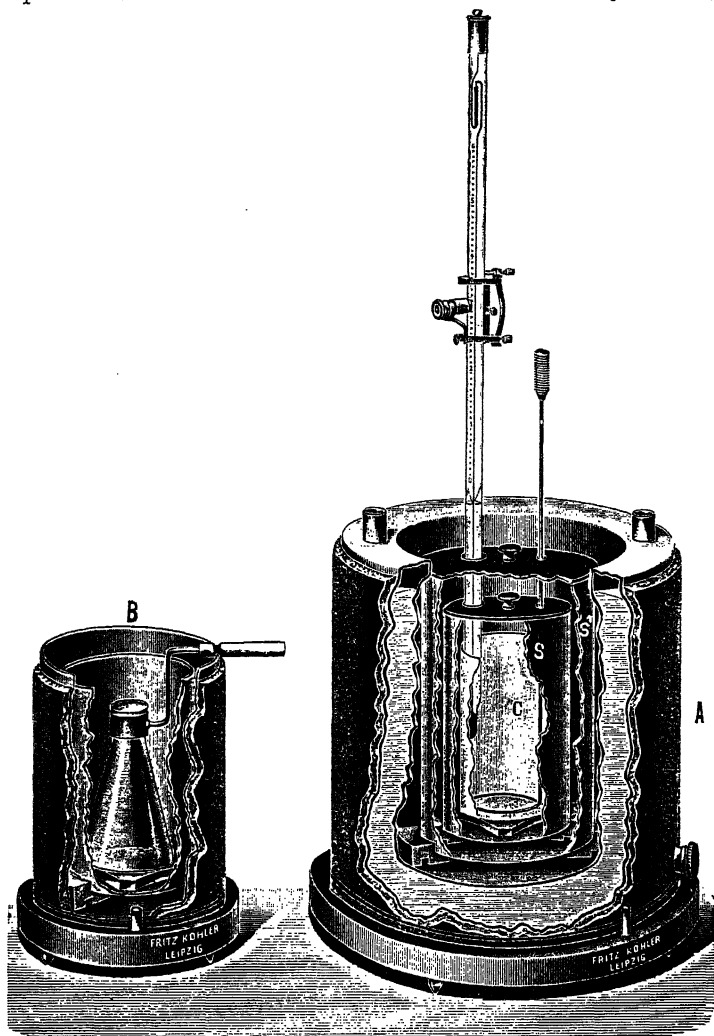
FIG. 108.

and polished metal vessels, and by a double-walled vessel filled with water. The different vessels are insulated from one another by wooden blocks (Fig. 108, A).

The change of temperature produced in the water or other liquid contained in the calorimeter is measured by means of a thermometer graduated in hundredths of a degree, and the temperature throughout the liquid is kept uniform by means of a metal stirrer. The calorimeter and surrounding cylinders should also be covered by non-conducting lids, in order to prevent air-currents and evaporation of the liquid in the calorimeter. The lids are suitably cut to allow of the passage of the thermometer and stirrer.

Units.—Various units are employed in which to express the amount of heat. One of the oldest units is the amount of heat required to raise the temperature of 1 gram of water from 15°–16° c. This quantity of heat is called the calorie (or gram-calorie), and is represented by cal. Since this unit is rather small, and since the expression of heats of reaction in this unit would lead to the use of very large numbers, a larger unit is now frequently used, viz. the kilogram-calorie (kg.-cal.), which is equal to 1000 small or gram calories.

In many cases, especially where calculations of transformation of energy are involved, it is better to employ absolute units. In this system, the unit of energy is called an *erg*, and the value of 1 cal. is $4 \cdot 185 \times 10^7$ ergs. Since 1 joule is equal to 1×10^7 ergs, it follows that 1 cal. is equal to $4 \cdot 185$ joules ; or 1 kg.-cal.$=4 \cdot 185$ kilojoules (*kj*), or 1 *kj*$=0 \cdot 2390$ kg.-cal.

A.—Heat of Neutralization of Acids and Bases in Dilute Solution

According to the theory of electrolytic dissociation, the molecules of acids, bases, and salts, in aqueous solution, are regarded as undergoing ionization to a greater or less extent. If this ionization were complete, then the process of neutralization, say of hydrochloric acid by caustic soda, could be represented by the equation, $H^{\cdot} + Cl' + Na^{\cdot} + OH' = Na^{\cdot} + Cl' + H_2O$. That is to say, the process would consist merely in the combination of hydrogen ion and hydroxide ion to form (practically) un-ionized water. This may be regarded as sufficiently near to the truth in the case of strong acids and alkalis in fairly dilute solution ; and consequently, in such cases, the heat of neutralization will be the same for all acids and alkalis, viz. 13,800 cal. In the case of weak acids or

weak alkalis, however, ionization may be far from complete, so that, on neutralization, the heat effect will involve not only the heat of combination of hydrogen ion and hydroxide ion, but also the heat of ionization of the weak acid or alkali. The heat of neutralization in such cases will, therefore, be either greater or less than 13,800 cal., according as ionization of the alkali or acid is accompanied by an evolution or absorption of heat.

In illustration of what has been said, the following experiments should be performed.

EXPERIMENT.—*Determine the Heat of Neutralization of Hydrochloric Acid by Sodium Hydroxide.*

Prepare approximately 0·25N solutions of hydrochloric acid and of sodium hydroxide, free from carbonate (see p. 180), and determine their concentration by titration.

Fit together the calorimeter and its protecting vessels (all well polished), as shown in Fig. 108, the outer vessel having been filled with water some hours previously in order that it may acquire, as nearly as possible, the temperature of the room. A Beckmann thermometer, previously set (p. 129) so that the mercury stands at the lower end of the scale at the temperature of the room, is passed through the holes in the covers of the calorimeter and supported so that the bulb passes about two-thirds down the calorimeter. The calorimeter is also furnished either with a simple ring stirrer to be worked by the hand, or, preferably, with a rotating screw stirrer to be worked by a small motor. In the latter case the rotation should be as uniform as possible, and not too rapid.

In the calorimeter are placed 250 ml. of the solution of caustic soda, while 250 ml. of the hydrochloric acid are placed in a flask surrounded by several polished metal cylinders to minimize changes of temperature by radiation (Fig. 108, B). A Beckmann thermometer is also supported in the acid solution.[1] The readings on this thermometer must be compared with those on the thermometer placed in the alkali, in order that it may be known whether the

[1] When the acid is afterwards poured into the alkali, a certain amount of it will, of course, remain adhering to the walls of the flask and to the thermometer. This amount can be determined by titration ; but the necessity for this can be avoided by first wetting the flask and thermometer with the acid solution, and then pouring in 250 ml. of the acid solution. In this way practically the same amount of acid will be introduced into the flask at the beginning as is left after the acid has been poured into the alkali.

temperature of the acid and alkali is the same at the time of mixing ; or, if not, what the difference of temperature is.

Since, either before or after the addition of the acid to the alkali, the temperature of the liquid in the calorimeter must be different from atmospheric temperature, it follows that there will be an interchange of heat between the calorimeter and the outside. As this can introduce a not inconsiderable error into the measurement, allowance for the heat lost or gained by radiation must be made. One way in which the error can be minimized is to arrange that the acid and alkali, before mixing, are at a temperature as much below that of the room as the mixture will be above room temperature. The amount of heat gained from the outside will then be approximately the same as that lost by radiation from the calorimeter.

A better method, however, is the following : The temperatures registered by the thermometers immersed in the acid and alkali should be read, say every minute, for at least five minutes before the mixing of the solutions takes place. During this time the solutions should be stirred quietly. Then, at a particular moment, which must be noted, the acid is poured as rapidly as possible into the alkali, the two solutions mixed well, and the temperature of the mixture read every half-minute or every minute for five or ten minutes after mixing took place, until it is found that the fall of temperature becomes uniform. At first the temperature rises rapidly, then more slowly, and then begins to fall. Since, as the temperature rises above that of the room, radiation from the calorimeter is taking place, it follows that the highest temperature read will be lower than if no loss of heat by the calorimeter occurred. In order, therefore, to get the true elevation of temperature produced by the heat of neutralization, the temperatures read on the thermometer before and after mixing should be plotted on squared paper, the thermometer readings being represented as ordinates and the time as abscissæ. In this way two figures similar to those shown in Fig. 109 will be obtained.

In this figure the temperature of acid and alkali is represented as rising slowly previous to mixing ; but the reverse may, of course, also be found. If the time of mixing was, say, at the sixth minute, the temperature (t_1 or t_1') which the alkali and acid would have at that moment is

obtained by drawing a line through the different temperature readings and producing it to cut the perpendicular at the sixth minute (point a or a') ; and the highest temperature (t_2) which would have been reached in the absence of radiation is obtained by drawing a straight line through the last readings (when the fall of temperature has become uniform), and producing this line back so as to cut the perpendicular at the sixth minute. This gives the point b. The distance ab then gives the elevation of temperature required (t_2-t_1).[1]
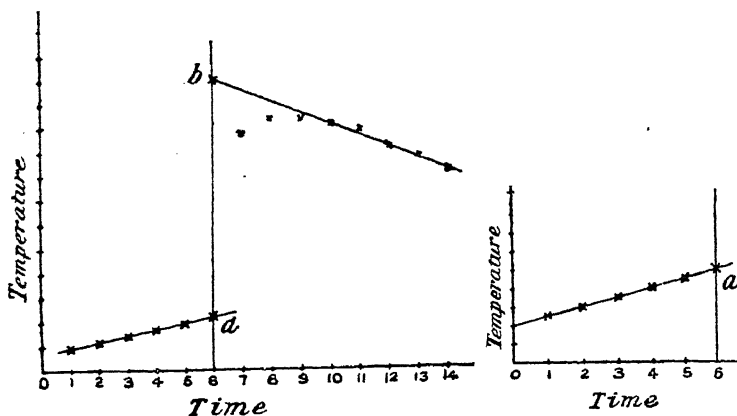
FIG. 109.

Calculation of the Heat of Neutralization.—As is shown in text-books on Physics, the heat produced in the reaction must be equal to the heat required to raise the solution, the calorimeter, the thermometer, and the stirrer through the range of temperature t_2-t_1 degrees. This, however, is equal to the sum of the masses of the different parts multiplied by their specific heat. For the heat evolved on mixing the acid and alkali, therefore, one has—

$$\text{heat evolved}=(m_1s_1+m_2s_2+m_3s_3+m_4s_4)(t_2-t_1)$$

[1] To render the correction for radiation unnecessary, the temperature of the bath surrounding the calorimeter may be regulated so as to follow the change in temperature of the reaction mixture in the calorimeter. See Richards and Forbes, *Proc. Amer. Acad.*, 1905, **41**, 3 ; Richards, Henderson and Frevert, *ibid.*, 1907, **42**, 573 ; Benedict and Higgins, *J. Amer. Chem. Soc.*, 1910, **32**, 461 ; Gray, *J. Chem. Soc.*, 1914, **105**, 1010. For the description of a synthermal regulator to ensure the same temperature in the calorimeter and surrounding bath, see Richards and Osgood, *J. Amer. Chem. Soc.*, 1915, **37**, 1718. See also Lange and Robinson, *Chem. Rev.*, 1931, **9**, 89.

where m_1, m_2, m_3, m_4 are the masses of the solution, calorimeter, thermometer, and stirrer respectively, and s_1, s_2, s_3, s_4 their specific heats. The following table gives the specific heat of the usual metals employed for calorimeter or stirrer :—

Platinum	.	.	.	.	.	.	.	.	.	0·032
Silver	.	.	.	.	.	.	.	.	.	0·056
Brass	.	.	.	.	.	.	.	.	.	0·092
Nickel	.	.	.	.	.	.	.	.	.	0·109

As regards the specific heat of the solution, this will vary more or less from that of pure water according to the concentration of the dissolved salt. With solutions of the concentration used above, it will be sufficiently accurate for present purposes to take the water-equivalent of the solution (*i.e.* its mass multiplied by its specific heat), as being equal to that of the *water* contained in it.

In the case of the thermometer, which consists of glass and mercury, the weight of which cannot be determined separately, the water-equivalent is obtained by making use of the fact that the specific heat of equal *volumes* of glass and mercury is practically the same and equal to 0·47 per millilitre. To obtain the volume, a beaker of water is counterpoised on the balance, and the thermometer then supported on a stand so that the bulb is immersed in the water. The weight which has now to be added in order to obtain equipoise gives the volume of the bulb. In the case of the Beckmann thermometer, the stem above the bulb is not solid, so that the external volume does not represent the volume of the glass and mercury. The external volume of the stem, so far as it was immersed in the solution during the experiment, should be determined separately from that of the bulb, and about one-fifth of the volume so obtained taken as the volume of the glass and mercury.

Considering that the acid and alkali do not behave as if they were completely ionized, and that the specific heat of the solution is only approximately estimated, the result of the measurement carried out in the manner described, may deviate from the value 13,800 cal. by about 200 cal.

Further Experiments.—In the manner described above, one should also determine the heat of neutralization of a weak base (ammonium hydroxide) with a strong acid (hydrochloric acid), and of a strong base (sodium hydroxide) with a weak acid (acetic acid). Determine also the heat of neutralization of phosphoric acid, using 1, 2 and 3 gram-molecules of sodium hydroxide per gram-molecule of phosphoric acid.

PROBLEMS

1. From the heat of neutralization of ammonium hydroxide by hydrochloric acid, and of sodium hydroxide by acetic acid, combined with the value obtained for the heat of neutralization of sodium hydroxide by hydrochloric acid, calculate the heat of ionization of ammonium hydroxide and of acetic acid. It may be assumed that in the dilutions employed, these substances are completely un-ionized.

2. Find what percentage error will be introduced into the result of the preceding calculation, if there was an error of ± 1 per cent. in the determination of the heats of neutralization.

B.—HEAT OF SOLUTION

The heat of solution of a solid or liquid substance can be determined in practically the same manner as that employed for the determination of the heat of neutralization, and the same apparatus can be employed. Since the heat which is evolved or absorbed on dissolving a substance depends on the amount of water or other solvent employed, the statement of the heat of solution has a definite meaning only when the concentration of the solution formed is given. If the dilution is so great that further dilution is unaccompanied by any heat effect, then the heat measured per gram-molecule of solute is known as the heat of solution at infinite dilution. Usually, however, it will not be possible to determine this heat of solution directly, and one must therefore state the number of gram-molecules of water in which one gram-molecule of solute is dissolved.

EXPERIMENT.—*Determine the Heat of Solution of Potassium Nitrate.*

A quantity of the salt, about 15 g., is finely powdered and placed in a test-tube. The latter is weighed, and then placed in a beaker of water surrounded by the protecting cylinders (Fig. 108, B), and the temperature of the water noted. In the calorimeter are placed about 500 g. of distilled water, and the apparatus then fitted together with thermometer and stirrer as described on p. 274. The same precautions as before as regards temperature readings are taken.

When the salt has taken the temperature of the water (say after 10 to 15 minutes), the tube is removed, roughly dried, and the contents emptied into the water in the calorimeter. Since the accuracy of the determination depends to a considerable extent on the rapidity with which the solid

dissolves, it is of importance that the salt should have been finely powdered, and that the stirring should be fairly vigorous. In this case a motor-driven stirrer is preferable to a hand-stirrer. The weight of salt taken is determined by weighing the tube before and after the addition of salt to the water.

In the above method, it may of course happen that the salt has not the same temperature as the water, so that a knowledge of the specific heat would be necessary. When this is known, then the heat given to or taken from the solvent by the salt, owing to the difference of temperature, can be easily calculated ; but even where the specific heat of the solid is not known, no great error will, in most cases, be made, unless the temperature difference between the solid and the solvent is considerable. By alteration of the temperature of the water in which the tube of salt is immersed, it will not be difficult to arrange that the difference of temperature between the solid and the solvent is very small.

In determining the heat of solution of salts, attention must be paid to whether they are anhydrous or hydrated ; and in the latter case, to the degree of hydration. Different values for the heat of solution will be obtained according to the state of the solid as regards these factors.

For the sake of comparison, the heat of solution of some of the commoner salts is given in the following table :—

Salt.	Number of gram-molecules of water to 1 gram-molecule of salt.	Heat of solution, kg.-cal.
KCl	200	− 4·4
KNO$_3$	200	− 8·5
ZnSO$_4$	400	+18·5
ZnSO$_4$.7H$_2$O . . .	400	− 4·24
CuSO$_4$	300	+15·8
CuSO$_4$5H$_2$O . . .	300	− 2·7

C.—HEAT OF COMBUSTION

By the heat of combustion of a substance is meant the amount of heat evolved in the combustion of 1 gram-molecule of the substance. If m be the mass of substance burned, the molecular weight of which is M ; and if W and w represent the weight of water and the water-equivalent of the appara-

tus respectively; and if $(t'-t)$ represents the rise of temperature produced by the combustion; then the heat of combustion is given by—

$$Q = \frac{M}{m}(W+w)(t'-t) \text{ calories}$$

The heat of combustion is best determined by the method due to Berthelot, which consists in burning the substance in an atmosphere of compressed oxygen. The original design of the autoclave in which the combustion takes

place (the Berthelot bomb) has been modified in various ways; and the form to be described here is the modification due to Mahler and to Kroeker.[1]

The Bomb.—The bomb consists of a steel vessel, the interior of which is enamelled, and is fitted with a lid lined on the under surface with platinum foil (Fig. 110). To ensure an air-tight junction, the lid is screwed firmly down on a lead washer. The lid is pierced by two channels—K_2, through which the bomb is filled with oxygen, and K_1, through which the gaseous products of combustion can be allowed to escape. Both these channels can be closed by means of the screw spindles V_2 and V_1. The continuation of the channel K_2 is formed by the platinum tube R, to which a platinum crucible, T, is attached for receiving the substance to be burned. The ignition of the substance is effected by means of a piece of iron wire, which is caused to burn by means of an electric current.[2] This wire is attached to the small pin a_2 on the tube R, and to the wire D. The current is led from a battery to these two poles, by wires clamped in the terminals P_1 and P_2. The screws S_1 and S_2 serve merely to close the lateral channels while the bomb is immersed in the water of the calorimeter.

FIG. 110.

[1] For many purposes the Griffin-Sutton bomb is very convenient (*J. Sci. Instr.*, 1933, **10**, 9, 286).
[2] One may also use a fine platinum wire which is heated by the current to incandescence.

The Calorimeter.—The heat of combustion is measured by the elevation of temperature produced in a given weight of water in a calorimeter. The calorimeter used for this purpose is essentially the same as that previously described

FIG. 111.

(p. 271). It consists (Fig. 111) of a large nickel-plated metal vessel, G, containing the water in which the bomb is immersed, and of a water-mantle, W. The water in the jacket can be stirred by means of the stirrers R, R, and the water of the calorimeter by the stirrer r, which can be worked by

hand, or driven by a motor. The stroke of the stirrer should be so arranged that at its lowest point it almost touches the bottom of the calorimeter, and at its highest point rises almost to, but not above, the surface of the water.

The rise of temperature is determined by means of a Beckmann or ordinary thermometer, graduated in hundredths of a degree. As it would be a matter of great inconvenience to determine the water-equivalent of the thermometer, stirrer, etc., separately, it is best to determine the water-equivalent of the whole apparatus subject to change of temperature, by finding the elevation of temperature produced on burning a weighed quantity of a substance the heat of combustion of which is known. For this purpose benzoic acid is used, the heat of combustion of which is 6324 cal. per gram.

Making a Determination.—The substance to be burned is first compressed into a pellet, and, after being weighed, is placed in the platinum crucible T. A piece of fine iron wire, about one-tenth of a millimetre in diameter and 6–7 cm. in length, is weighed, and its ends twisted round the wire D and the pin a_2. The middle portion of the wire should be formed into a narrow spiral by twisting it round a pin. When the wire is attached, raise the crucible until the middle portion of the iron ignition wire touches the pellet of compressed substance. After having coated the lead washer and the screw on the bomb with vaseline, the cover is tightly screwed down with the help of a large spanner, the bomb being meanwhile fixed in its holder. Be very careful that no grit gets either on the lead washer or in the screw of the bomb. The latter is now ready to be filled with oxygen.

Connect a cylinder of compressed oxygen with a manometer, and the latter, after removing the screw S_2, with the lateral channel of the bomb leading to the valve K_2. Open the valves V_2 and V_1 and allow oxygen to stream through the bomb for a short time. Then close the valve V_1 and continue passing oxygen into the bomb until the pressure registered on the manometer is 20–25 atmospheres. Now close the valve K_2, disconnect the tube from the manometer, and replace S_2. If there is any leakage of gas, it will generally make itself known by a slight hissing sound.

The calorimeter may now be got ready. The water-mantle having been filled with water (preferably some hours previously), a thermometer is hung in the air-space inside.

After it has taken the temperature of the enclosure, the temperature is read. A Beckmann thermometer, if one is used, is now set (p. 129) so that the lower end of the scale represents a temperature of about 1·5–2 degrees *below* that found in the enclosure of the water-mantle.

The calorimeter vessel is then tared, a quantity of water placed in it, and the weight of the water determined on a balance accurate to about 1 g. The amount of water used should be such that when the bomb is immersed, the water rises up to the level of the screws S_1, S_2. This must have been determined beforehand.

In order to reduce the error due to radiation, the temperature of the water in the calorimeter should be such that, before the combustion in the bomb occurs, it is about as much below the surrounding temperature (temperature of the air-space) as it will be above it, after the combustion has taken place. As the rise of temperature should be about 2·5° to 3°, the temperature of the water should be made about 1·5° lower than that of its surroundings.

The charged bomb is now lowered into the water of the calorimeter, with the help of a stout cord passed through the hole in the middle pillar on the cover of the bomb. The wires from a battery [1] are then connected with the screws P_1, P_2, and the lid of the calorimeter placed in position. Insert the thermometer through the cover of the calorimeter and set the stirrer in motion, at such a rate that it rises and falls about once per second. After the bomb has been in the water about five minutes, commence reading the temperature on the thermometer, readings being made every minute for about ten minutes. At the tenth minute close the electric circuit by means of a switch key. The iron wire will thereby be caused to burn and will ignite the substance in the crucible. The temperature of the water in the calorimeter will now begin to rise rapidly. Again take readings of the temperature, minute by minute (it will probably be impossible to make a reading at the first minute after ignition), until the highest temperature is reached, a point which must be carefully noted. The temperature will now begin to fall slowly, and readings at intervals of a minute must again be made for about ten minutes.

[1] The potential employed must be such as to cause the iron wire to take fire in the course of one or two seconds. This must be ascertained by a separate experiment.

By means of the graphical method described on p. 275, the rise of temperature which would have been produced if no radiation occurred, can be obtained. Use may also be made of an adiabatic calorimeter in which the temperature of the jacket is kept the same as that of the water in the calorimeter (p. 276, footnote).

This completes the series of observations. The bomb is removed from the calorimeter and carefully dried. Screw S_1 is removed, and the valve K_1 slowly opened so as to allow the gases to escape from the bomb. When the pressure has fallen again to that of the atmosphere, the cover is removed and the interior of the bomb cleaned and dried. Any of the iron wire which has not been oxidized should be detached and weighed, and the weight subtracted from that originally taken.

The water-equivalent of the bomb, stirrer, thermometer, and calorimeter can now be calculated, as shown in the following example :—

$$\text{Weight of benzoic acid taken} = 0.8523 \text{ g.}$$
$$\text{Weight of iron wire} = 0.0252 \text{ g.}$$

Heat evolved by the combustion of the benzoic acid $\Big\} = 0.8523 \times 6324 = 5390 \text{ cal.}$

Heat evolved by the combustion of the iron wire $\Big\} = 0.0252 \times 1600 = 40.3 \text{ ,,}$

$$\text{Total heat evolved} = 5430.3 \text{ ,,}$$

$$\text{Rise of temperature produced} = 2.3425°$$

Weight of water which would have been raised $2.3425°$ by 5430.3 cal. $\Big\} = 2318.2 \text{ g.}$

$$\text{Weight of water taken} = 2000.0 \text{ g.}$$

$$\text{Water equivalent of bomb, etc.} = 318.2 \text{ g.}$$

Having determined the water-equivalent of the apparatus, the heat of combustion of a substance (say, cane sugar or naphthalene) can be determined. The determination is carried out exactly in the manner described above.[1] (Heat of combustion of cane sugar $= 3946$ cal., and of naphthalene $= 9613$ cal. per gram.)

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[1] For the determination of heats of combustion, see Richards and Barry, *J. Amer. Chem. Soc.*, 1915, **37**, 993 ; Richards and Davis, *ibid.*, 1917, **39**, 341. A list of heats of combustion is given by Kharasch, *J. Research Nat. Bur. Stand.*, 1929, **2**, 359.

CHAPTER XV

HETEROGENEOUS EQUILIBRIA

THE condition for equilibrium in heterogeneous systems is given by the phase rule : $F = C + 2 - P$, where F is the degree of freedom, C the number of components, and P the number of phases present. When $P = C + 2$, the system has no degrees of freedom ; the temperature and pressure under which it can exist are perfectly definite. If one of the variables, temperature or pressure, is fixed, then equilibrium will be definitely fixed when $P = C + 1$. Thus, if the pressure is fixed (say, atmospheric), then equilibrium between a solid and a liquid phase of a single substance will be defined by a definite temperature, namely, the melting-point.

Owing to the importance of heterogeneous equilibria, a number of different cases will be studied.

I.—VAPOUR PRESSURE OF SALT HYDRATES

A salt hydrate is a two-component system. When dehydration occurs a second solid phase, anhydrous salt or lower hydrate, is formed, and the system then consists of three phases—two solid phases and one vapour phase. The system is therefore univariant, and the vapour pressure will vary with the temperature. If, however, the temperature is kept constant, the vapour pressure will be constant. This vapour pressure may be measured, for example, by the dew-point method.[1]

EXPERIMENT.—*Determine the Vapour Pressure of Sodium Sulphate Decahydrate.*

The apparatus (Fig. 112) consists of a wide-mouthed bottle, B, which is closed by a rubber stopper. Through this stopper pass a closed tube of bright silver, A, and the glass tube C, which is furnished with a stop-cock. The mouth of the silver tube, also, is closed by a rubber stopper, through which pass a thermometer, T, graduated in tenths of a degree,

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[1] Cumming, *J. Chem. Soc.*, 1909, **95**, 1772; Hepburn, *Proc. Physical Soc.*, 1928, **40**, 249; *J. Chem. Soc.*, **1932**, 550.

and two narrow glass tubes. One of these reaches nearly to the bottom of the silver tube, the other only passes through the stopper. Before being used for an experiment, the silver tube, which must be brightly polished, is dipped in boiling-hot distilled water. In this way, a boundary-line is produced which becomes visible only when dew is deposited on the tube and which renders the deposit more easily detected.
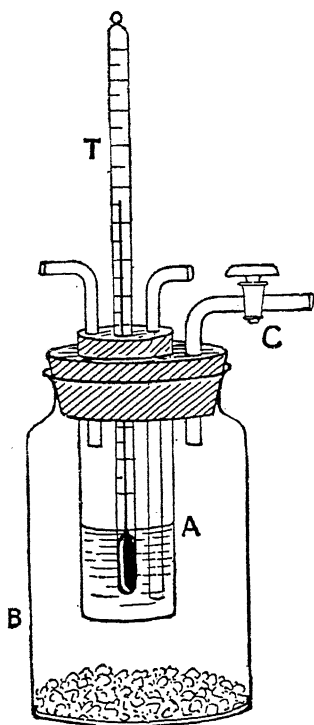
A quantity (10–15 grams) of roughly powdered sodium sulphate decahydrate is placed at the bottom of the dry bottle, B, and the rubber stopper, carrying its silver and glass tubes, is placed firmly in position. A quantity of ether is poured into the silver tube which is then stoppered, and the bottle is supported in a beaker of water, the temperature of which is maintained constant at, say, 20° or 25°. Tube C is connected with a water-pump and the bottle is partially exhausted. The stopcock on C is then closed.

When the bottle and its contents have taken the temperature of the bath, air is blown through the ether by means of a rubber bulb tube. The ether is thereby caused to evaporate

FIG. 112.

rapidly, and the temperature of the silver tube falls. Note the temperature at which a film of dew appears on the silver tube. Stop evaporating the ether, allow the temperature of the silver tube to rise, and note the point at which the film of dew disappears. Several readings of the appearance and disappearance of the dew should be made, and the mean taken. This is the dew-point. From the tables of vapour pressure of water, the pressure corresponding to the dew-point is obtained, and this gives the vapour pressure of the system $Na_2SO_4,10H_2O — Na_2SO_4 — H_2O$ (vapour) at the temperature of the bath.

In the same way, one may determine the dissociation pressures of $CuSO_4,5H_2O$ and of $MgSO_4,7H_2O$ at, say, 20°–30°. The method may also be used to determine the vapour pressure of aqueous solutions.

The vapour pressure of a hydrate may also be determined by finding the concentration of a solution of sulphuric acid with which the hydrate is in equilibrium.[1] The vapour pressure of the solution can be obtained from tables.

II.—Determination of Solubility

The property of forming solutions or homogeneous mixtures of varying composition, is a very important one, and is met with in all three physical states of matter, gaseous, liquid, solid. Of the different possible kinds of solutions, the most important are those formed by the solution of a gas in a liquid, of a liquid in a liquid, and of a solid in a liquid.

Solubility of a Gas in a Liquid

In the equilibrium between a gas and a liquid, only two phases are present—the system, therefore, is bivariant. In order that the condition of equilibrium may be defined, it is necessary to fix two of the independent variables, temperature and pressure.

The solubility of a gas in a liquid can readily be determined by means of the apparatus shown in Fig. 113, except in those cases where the gas is very soluble (ammonia-hydrogen chloride, etc.).[2] In its essential parts, the apparatus consists of a gas measuring burette, A, connected with a levelling tube, B. The burette is furnished with a three-way tap, a, which connects, on the one side, with the gas supply, and on the other, with a tube leading to the "absorption pipette" C, also furnished with the three-way tap b and an ordinary tap, c. Care should
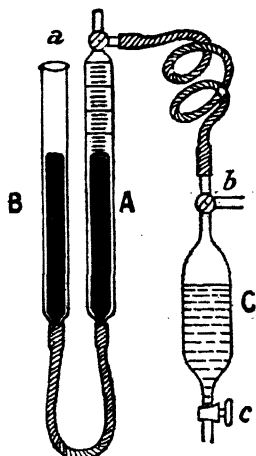
FIG. 113.

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[1] Collins and Menzies, *J. Phys. Chem.*, 1936, **40**, 379.

[2] See Geffcken, *Z. physikal. Chem.*, 1904, **49**, 298; Findlay and Creighton, *J. Chem. Soc.*, 1910, **97**, 536. See also van Slyke, *J. Biol. Chem.*, 1939, **130**, 545.

be taken in selecting these taps to see that they fit closely. The gas burette and absorption pipette are connected by a length of lead or, preferably, of copper tubing of narrow bore (about 1 mm.). This tubing is best wound into a spiral, so as to give flexibility to the apparatus, and allow of the absorption pipette being shaken.

For the purpose of joining the glass and metal tubes, the following device can be employed. To the metal tube is soldered a piece of brass tubing about 2 inches long, and sufficiently wide to take the glass tube (Fig. 114). A quantity of sealing wax or hard pitch is
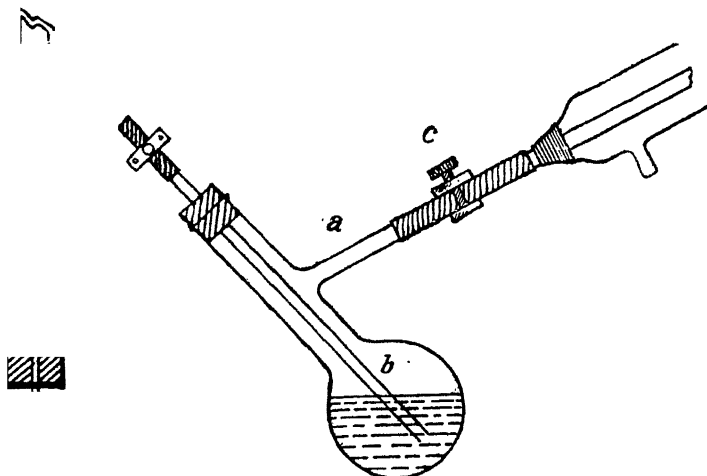
FIG. 114.   FIG. 115.

melted inside the brass tube and the glass tube then inserted, so that the end of the metal capillary passes inside the glass tube. If necessary, the joint can be further strengthened by an external coating of sealing wax.

Before carrying out a determination, the volume of the absorption pipette between the two taps must first be determined by means of water or mercury. For the solubility of gases such as carbon dioxide, the pipette may suitably have a volume of about 100 ml. For less soluble gases, the volume should be greater.

The solvent to be used for the absorption of the gas must first be rendered air-free. This is best done by boiling the liquid for some time in a flask with reflux condenser attached. The flask is best fitted up as shown in Fig. 115. The side

tube, a, of the round-bottomed distilling flask is connected with a condenser by means of a piece of rubber tubing having a screw clip, c. Through a rubber stopper in the neck of the flask passes a glass tube, b, which reaches nearly to the bottom of the flask. The other end of the tube is closed by rubber tubing and a clip.

While the liquid is being boiled, the clip on the tube b is closed, while there is free connection with the condenser. After the liquid has been boiled sufficiently long (10–15 mins.), the clip c is closed and the flame at the same time removed. After the liquid has cooled down to the ordinary temperature the flask is inverted and connected, by means of the side tube, with the lower outlet tube of the absorption pipette. The absorption pipette is exhausted by means of a pump attached to the tube b of the absorption pipette and the taps then closed. The clip on the tube b of the distillation flask is now opened in order to bring the interior of the flask to atmospheric pressure, and then, *as soon as possible*, the clip c is opened and also the lower tap of the absorption pipette. The solvent is then drawn into the pipette from the bottom of the liquid in the boiling flask, to which the air admitted into the flask will not have had time to diffuse.

EXPERIMENT.—*Determine the Solubility of Carbon Dioxide in Water at 25°.*

The apparatus having been fitted together, the absorption pipette, filled with air-free water, is placed in a thermostat at 25°. The mercury in the measuring burette is raised until it completely fills the burette, and a current of moist carbon dioxide from a Kipp apparatus is allowed to pass through the metal connecting tube and to escape into the air through the three-way tap on the absorption pipette. When all the air has been swept out, the tap a is turned and the burette filled with carbon dioxide. After adjusting the levels of the mercury, the volume is read off. A slight increase of pressure is now established in the burette and the tap a turned so as to make connection between the burette and the pipette. The tap c of the pipette is opened and then the tap b, and a certain amount (say 20–30 ml.) of water allowed to run out into a flask. The weight of water run out is then determined. The volume of the water in the pipette, and also the air-space, can thus be calculated, since the total volume of the pipette is known.

The pipette is replaced in the thermostat and is shaken

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carefully from time to time, the gas in the burette being always in communication with the pipette. As absorption of the gas proceeds, the levelling tube of the burette is raised so as always to maintain the gas at atmospheric pressure. When the absorption of gas ceases, the volume left in the burette is read off.

If the solubility of a gas in a liquid is defined by the ratio of the volume of gas absorbed to that of the absorbing liquid, one obtains—

$$S = \frac{v_1\left(\dfrac{P_1-p_1}{P_2-p_2}\cdot\dfrac{T_3}{T_1}\right)-v_2\left(\dfrac{P_2-p_1}{P_2-p_2}\cdot\dfrac{T_3}{T_2}\right)-V_1}{V_2}$$

where v_1 is the initial and v_2 the final volume of gas in the burette ; P_1 is the initial and P_2 the final barometric pressure ; p_1 is the partial pressure of the water vapour at the initial absolute temperature of the burette and p_2 the partial pressure at the temperature of the thermostat ; T_1 is the initial and T_2 the final absolute temperature of the burette, and T_3 the absolute temperature of the thermostat ; V_1 is the volume of the gas space and V_2 the volume of the liquid in the pipette.

Instead of filling the burette with moist gas, it is better first to dry the gas by means of phosphorus pentoxide. When dry gas is employed in the burette, a short tube of phosphorus pentoxide should be inserted between the metal connecting tube and the absorption pipette. Also, the three-way tap of the absorption pipette should be kept closed except just when it is necessary to allow gas to pass from the burette to the pipette. Under these conditions, the solubility is given by the expression

$$\left[(v_1-v_2)\,\frac{P}{P-p_2}\cdot\frac{T_3}{T_1}\right]-V_1$$

The barometric pressure is supposed not to change during the experiment.

The solubility of carbon dioxide in water at $25°$ is equal to $0·82$.

SOLUBILITY OF A LIQUID IN A LIQUID

When ether is shaken with water, a certain definite amount of the ether dissolves in the water, and similarly a

definite amount of water dissolves in the ether. One thus obtains two liquid solutions the composition of which depends on the temperature. At each temperature, therefore, there will be two solubility values, one representing the solubility of ether in water, and the other the solubility of water in ether.

When the liquids are such that the amount of one of them can conveniently be determined by analysis, the mutual solubility curve is easily determined. For this purpose the two liquids are shaken together in a stoppered bottle immersed in a thermostat. The bottle is then allowed to remain undisturbed until the two liquid layers have separated. A quantity of each layer is then pipetted out, weighed, and the amount of one of the components determined by analysis. Such a method, for example, can be employed in the case of aniline and water, the aniline being titrated by means of a solution of potassium bromate and bromide of known concentration. Similarly, also, with phenol and water.

In most cases, however, the analytical method is not applicable,[1] and it is therefore necessary to employ the synthetic method. To carry out this method, weighed amounts of the two components are placed in a small glass tube, and the end of the tube then drawn out and sealed off. So long as two liquid layers are present, a turbid liquid is formed on shaking the tube, but at the temperature at which one of the layers just disappears, this turbidity also disappears, and a single homogeneous solution is now obtained which represents a saturated solution of one of the liquids in the other. Since the composition of the solution and the temperature at which the turbidity disappears are known, a point is obtained on the mutual solubility curve of the two liquids. By varying the initial amounts of the two liquids, the complete solubility curve can be determined.[2]

EXPERIMENT.—*Determine the Mutual Solubility Curve of Phenol and Water.*

A number of tubes are prepared about 10 cm. long and 1 cm. wide, and with a constriction near the open end, as shown in Fig. 116, A. Or, in place of these, one may obtain

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[1] In some cases the composition of the solution may be determined by vapour density measurements (p. 59).
[2] For solubilities of liquids in liquids, see Rothmund, *Z. physikal. Chem.*, 1898, **26**, 475 ; Timmermans, *ibid.*, 1907, **58**, 129.

tubes fitted with a stopper, which can be held in place by means of two springs, as in Fig. 116, B.

Into these tubes are introduced, by means of narrow-stemmed pipettes or funnels, different relative amounts of phenol and water, the weights of which are determined. The tubes are placed in holders, formed, for example, of stout copper wire, and are immersed successively in a large beaker full of water, in which also is a thermometer graduated in tenths of a degree. The temperature of the water is caused to rise, and during this time, the tube with the two liquids is shaken at frequent intervals. At first the temperature may be allowed to rise rapidly until the turbidity shows signs of disappearing; after which the temperature must be raised only slowly, and the tube be frequently shaken. At the moment when the turbidity disappears on shaking, the temperature is read. The temperature of the bath is now allowed to fall very slowly, and the point is noted at which the turbidity just begins to appear once more. The experiment is repeated once or twice, and the mean of the temperatures at which the turbidity disappears on heating and reappears on cooling, is taken as the temperature at which phenol and water, in the particular proportions taken, become completely miscible. In a similar manner the temperatures are obtained for other mixtures of phenol and water. The results are then plotted with percentage amount of one component as abscissæ against temperatures at which homogeneity occurs, as ordinates, and a smooth curve is drawn through these points. The maximum temperature point on the curve is known as the *critical solution temperature*.
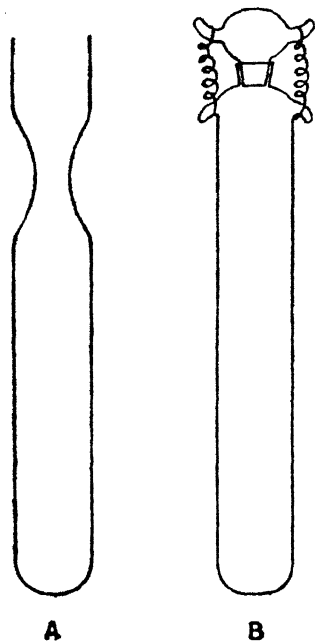
This critical solution temperature is very greatly influenced by the presence of impurities, and this fact may

A   B

FIG. 116.

be made use of for the purpose of detecting the presence of impurities, or, in other words, as a criterion of purity.

EXPERIMENT.—*Determine the Effect of Impurity on the Critical Solution Temperature of Phenol and Water.*

Having determined, as above, the mutual solubility curve and the critical solution temperature of pure phenol and water, similar experiments should be carried out using water and phenol to which about 0·5 to 1 per cent. of sodium chloride has been added ; or the sodium chloride may be dissolved in the water. The experiments may be confined to mixtures containing from about 20–50 per cent. of phenol.

Additional Experiments may be carried out with the following pairs of liquids : iso-butyric acid and water, hexane and methyl alcohol, carbon disulphide and methyl alcohol, acetylacetone and water.

Three Component Systems.—The experiment which has just been described shows that the mutual solubility of a pair of partially miscible liquids may be markedly altered by the addition of a third component. In general, when the third component is soluble in only one of the other two components, the mutual solubility of the two liquids is diminished ; but when the third component dissolves readily in each of the other two components, the mutual solubility of the latter is increased. This behaviour is illustrated by the system chloroform, water, acetic acid. When acetic acid is added to a heterogeneous mixture of chloroform and water, at a definite temperature, the mutual solubility of these two liquids is increased, and a point is reached at which the mixture becomes homogeneous. The amount of acetic acid which must be added to bring about homogeneity at the given temperature, will depend on the relative proportions of chloroform and water in the original mixture. Similarly, when water is added to a homogeneous mixture of chloroform and acetic acid (two completely miscible liquids), a heterogeneous mixture (two liquid solutions) will be formed when a certain amount of water, depending on the initial composition of the mixture, has been added.

To illustrate this behaviour, the following experiment may be carried out.[1]

Mixtures of chloroform and acetic acid of varying com-

[1] See Wright, *Proc. Roy. Soc.,* 1891, **49**, 174 ; 1892, **50**, 375.

position are made up in a set of five stoppered bottles of 70–80 ml. capacity. These mixtures may suitably contain 10, 20, 40, 60 and 80 p.c. of chloroform by weight respectively. Since the densities of chloroform and acetic acid are 1·50 and 1·05 respectively, the mixtures may be prepared by running into the bottles from burettes, the following volumes of chloroform and acetic acid :

| Chloroform | 1·67 | 3·33 | 6·66 | 9·99 | 13·32 ml. |
| Acetic Acid | 21·43 | 19·05 | 14·30 | 9·53 | 4·77 ml. |

The bottles containing the solutions are placed in a thermostat at 18° and after they have taken the temperature of the bath, water is run, in small quantities at a time, into each of the bottles in turn ; and after each addition, the bottle is well shaken. Addition of water is continued until, on shaking, a turbidity makes its appearance. The final additions of water should be made drop by drop, care being taken not to add too much water, especially in the case of the solutions richest in chloroform. From the amount of water added and the initial amounts of chloroform and acetic acid, the percentage, composition of the mixture, when turbidity makes its appearance, is calculated, and the results are plotted in a triangular diagram. The points obtained are joined by a smooth curve, which may be completed by means of the data :—

Saturated solution of water in chloroform contains 99 per cent. of chloroform.

Saturated solution of chloroform in water contains 0·8 per cent. of chloroform.

The triangular diagram usually consists of an equilateral triangle the length of whose side is taken as unity or 100, and represents, therefore, the sum of the fractional or percentage amounts of the three components ; and each corner of the triangle represents 100 p.c. of one of the components (Fig. 117). In plotting the composition of a ternary mixture, two points are marked on one side of the triangle, representing the percentage amounts of two components, and from these points lines are drawn parallel to the other two sides of the triangle. The point of intersection gives the composition of the ternary mixture.

Thus, to represent the composition, 15·1 p.c. of chloroform, 50·2 p.c. of acetic acid and 34·7 p.c. of water, the side of the triangle for chloroform and acetic acid (Fig. 117) is marked at the two points representing 15·1 p.c. of chloroform and 50·2 p.c. of acetic acid, and lines are drawn from these points parallel to the sides of the triangle. The point of intersection, x, represents the composition of the above ternary mixture.

The curve obtained by joining the experimentally determined points forms the boundary between homogeneous and heterogeneous mixtures. A mixture of chloroform, acetic acid and water represented by any point outside the curve, towards the acetic acid corner of the triangle, will form only one homogeneous solution ; while any mixture represented by a point within the curve will separate into two layers.

Additional Experiments.—The system benzene-acetic acid-water [1] may be studied at 25° in the manner described above.[2] Further, the boundary curve for chloroform, acetic acid and water may be
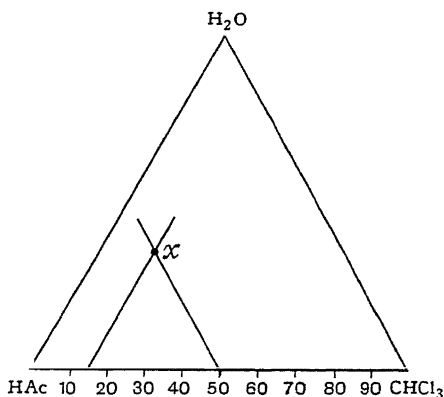
FIG. 117.

determined at a series of temperatures, and the curves plotted on the same triangular diagram. The construction of a three-dimensional model would also be instructive.

It will also be of interest to study, between 50° and 100°, the system water-phenol-aniline [3] and the system water-ether-succinic nitrile [4] at 60°.

SOLUBILITY OF SOLIDS IN LIQUIDS

When a solid is brought into contact with a liquid in which it can dissolve, a certain amount of it passes into

[1] Waddell, *J. Phys. Chem.*, 1898, **2**, 233.
[2] One may also prepare heterogeneous mixtures of known composition of benzene and water and add acetic acid from a burette until, on shaking the mixture, no turbidity is observed.
[3] Schreinemakers, *Z. physikal. Chem.*, 1899, **29**, 577.
[4] Schreinemakers, *ibid.*, 1898, **25**, 543 ; Holmes, *J. Chem. Soc.*, 1918, **113**, 263.

solution ; and the process continues until the concentration of the solute in the solution reaches a definite value independent of the amount of solid present. A condition of equilibrium is thus established between the solid and the solution ; the solution is *saturated*.

The condition of saturation, therefore, depends not only on the solvent, but also on the solute, or the solid phase in equilibrium with the solution ; so that in all determinations of the solubility it is necessary, not only to determine the amount of dissolved substance in the solution, but also to ascertain the character of the solid phase which is in equilibrium with the solution. The importance of this must ever be borne in mind.

The amount of substance dissolved depends, not only on the substance, but also on the temperature ; and the solubility of a substance, or the number of grams of substance dissolved by a given weight of the solvent, may either increase or decrease with rise of temperature. In all cases, however, whatever be its particular form, the solubility curve of any substance is continuous, so long as the solid phase, or solid substance in contact with the solution, remains unchanged. If, however, a change in the solid phase occurs, the solubility curve will show a " break " or discontinuous change in direction.

For the production of the equilibrium between a solid and a liquid, *i.e.* for the production of a saturated solution, time is necessary ; and the length of time required not only varies with the state of subdivision of the solid, and the efficiency of the shaking or stirring, but is also dependent on the nature of the substance. In all cases, therefore, care must be taken that sufficient time is allowed for equilibrium to be established ; more especially when changes in the solid phase may occur.

In cases where the solubility increases with rise of temperature, the time required for the attainment of equilibrium can generally be shortened by preparing a saturated solution at a higher temperature and allowing it to cool to the desired temperature in contact with the solid phase. Particular care, however, must be exercised in cases where the solid phase itself undergoes change with the temperature.

Determination of the Solubility.—The production of a saturated solution can be carried out very simply in the apparatus shown in Fig. 118. It consists of a tube, *a*, in which the solid and solvent vigorously stirred by means of

the glass screw stirrer shown at b. The stem of the latter passes through a glass tube, inserted in the rubber stopper by which the solubility tube is closed. The tube should be chosen of such a size that the stem of the stirrer just passes through, the bearing being well lubricated by means of vaseline.[1]

The progress of solution towards saturation can be tested by withdrawing some of the solution from time to time, and determining the amount of dissolved substance.[2] This requires only to be done once, the solution in other experiments being then well stirred for a period somewhat longer than that required for complete saturation.

When saturation has been effected, the solution must be analysed. The stirrer is removed from the tube, and the latter closed with an unbored cork, the solubility tube being meanwhile kept in the thermostat. After the solid has subsided, a known volume of the solution is transferred to a tared weighing bottle by means of a pipette, to the end of which is attached, by rubber tubing, a short glass tube filled with cotton-wool to act as a filter ; and the solution is then

FIG. 118.

weighed. The density of the solution can in this way be determined. The amount of solid in solution is determined in an appropriate manner, most simply (if allowable) by evaporation on the water-bath, and drying, if necessary, at a slightly higher temperature, or by gravimetric or volumetric analysis.

When the temperature of experiment is fairly high, it may be necessary to warm the pipette first before withdrawing the solution ; otherwise solid may separate out in the pipette.

[1] Another useful form of apparatus for the determination of solubility is described by Campbell, *J. Chem. Soc.*, **1930**, 179. See also Brönsted and La Mer, *J. Amer. Chem. Soc.*, 1924, **46**, 555.

[2] The process of solution can be followed very conveniently by determining the refractive index of the solution by means of the Abbe refractometer (p. 118).
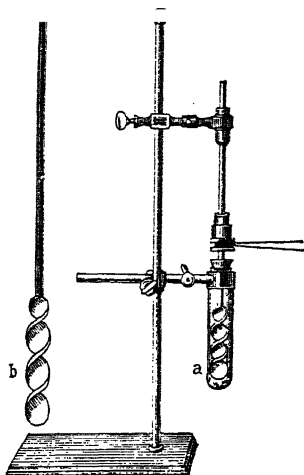
EXPERIMENT.—*Determine the Solubility of Potassium Chloride from* 10° *up to* 50°.

Fit up a thermostat and regulate the temperature so as to be at about 5°–8°, the variations of temperature being not greater than 0·1°. In the solubility tube (Fig. 118) place a quantity of *finely powdered* potassium chloride and water, and after fitting it with a stirrer, place it in the thermostat so that it is immersed up to the level of the cork. The solid and solution should now be stirred for 2–3 hours, and a quantity of the solution removed as described above, weighed, and evaporated to dryness.[1] To the solution in the tube add a further quantity of *finely powdered* potassium chloride, and allow the stirring to continue for another period of 1–2 hours. Again determine the composition of the solution. If this agrees with the former determination, it shows that the saturation was complete in the first period of 2–3 hours ; but if the amount of dissolved solid is greater in the second case, the stirring must be continued for some time longer, with addition, if necessary, of more potassium chloride, until the concentration of the solution becomes constant. This gives the solubility at the particular temperature of the experiment, and should be controlled by a second, independent determination. Express the solubility as grams of salt to 100 grams of water.

Having determined the solubility at a temperature between 5° and 8°, raise the temperature of the thermostat by 5° or 10°, and make another determination of the solubility at this higher temperature. Make further determinations at intervals of about 10°, up to 50°–55°. Instead of making two determinations at each temperature, as mentioned above, the first series of determinations can be controlled by approaching saturation from the side of super-saturation, *i.e.* by allowing the solution to cool down from a higher temperature *while in contact with the solid*. The solid phase must be present, and the solution should be stirred.

The results are then plotted in rectangular co-ordinates, the temperatures being plotted as abscissæ, and the solubility (grams of salt to 100 grams of water) as ordinates. Draw a smooth curve through the points so obtained, and from the curve read off the solubility at every five degrees.

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[1] The potassium chloride may also be determined by titration with silver nitrate.

When one applies van't Hoff's reaction isochore to solubilities, one obtains the expression, $\dfrac{d \log_e S}{dT} = \dfrac{Q}{RT^2}$, where S is the solubility in gram-molecules per litre and Q the heat of solution. Assuming (what is generally not quite true) that Q is independent of the temperature, this expression yields, on integration, $\log_{10} S_2 - \log_{10} S_1 = \dfrac{Q(T_2 - T_1)}{2\cdot303 \times 1\cdot99 \times T_2 \times T_1}$. From this expression the heat of solution can be calculated. Having calculated the value of Q, insert it in the above expression, and taking the value of S_1 at a temperature T_1, calculate the solubility at some other temperature, T_2. Compare the solubility so calculated with the experimentally determined value.

The value of Q calculated from the solubility may also be compared with the (different) heat of solution, determined calorimetrically (p. 278). Why do the values differ ?

Additional Exercise.—The solubility of benzoic acid may also be determined at temperatures between 20° and 60°. The amount of benzoic acid in a definite volume and weight of saturated solution can be determined by titration with 0·25N-NaOH, using phenol-phthalein as indicator, the solution of benzoic acid being first diluted as may be necessary. (Solubility at 20°=0·290, and at 60°, 1·155 g. per 100 g. of water.)

In the case of potassium chloride and benzoic acid, the solid phase remains unchanged throughout the whole range of temperature. A case may now be studied where the solid phase undergoes change.

EXPERIMENT.—*Determine the Solubility of Sodium Sulphate from* 10° *to* 50°.

The determinations of the solubility are carried out exactly as described above. Between 28° and 35°, determinations should be made at every two degrees. The results are then plotted graphically as before, the solubility being calculated in grams of *anhydrous* salt to 100 grams of water.

At the temperature of 30°, and also at the temperature of about 35°, the excess of solid in contact with the solution should be rapidly separated by filtration with the aid of a water-pump, using for the filtration merely a loose plug of cotton-wool in the stem of the funnel, or a filter of sintered glass may be used. The solid is then rapidly pressed between filter-paper, and the amount of water of crystallization determined in the ordinary way.

The solubility curves obtained from the above determinations should be produced so as to cut each other. The point of intersection gives the *transition point* of

$$Na_2SO_4.10H_2O \rightleftarrows Na_2SO_4 + 10H_2O$$
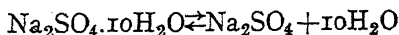
III.—DETERMINATION OF TRANSITION POINTS

It is a well-known fact that there are many substances which are capable of existing in more than one crystalline form, one of the best-known examples of this being sulphur. In general, these different polymorphous forms, as they are called, are not equally stable at a given temperature. Thus, at the ordinary temperatures, rhombic sulphur is the most stable form, and monoclinic sulphur, if kept sufficiently long, will change spontaneously into the rhombic. If, however, the temperature is raised to, say, 100°–110°, it is found that the monoclinic crystals can be kept indefinitely without undergoing change, while the rhombic crystals pass into monoclinic. At this temperature, therefore, the monoclinic is the most stable form. At a temperature of about 96°, it is found that both forms are equally stable, and that neither form changes into the other on keeping. This temperature is known as the *transition temperature*, or transition point. This point gives the temperature at which the relative stability of the polymorphous forms changes.

Not only are such transition points found in the case of polymorphous substances, but they are found, in general, also in the case of salt hydrates. When a salt combines with water to form one or more different hydrates, it is found that under given conditions of temperature, etc., only one of the hydrates, or it may be the anhydrous salt, is stable. Thus, on heating sodium sulphate decahydrate to above 33°, it is found that decomposition occurs into anhydrous sodium sulphate, and a saturated solution of this salt. On the other hand, on allowing a saturated solution of sodium sulphate to cool down in presence of anhydrous sodium sulphate, it is found that when the solution is cooled below about 33°, the anhydrous salt takes up water and forms crystals of the decahydrate. The temperature of (approximately) 33°, therefore, constitutes a transition point or inversion point for the change $Na_2SO_4.10H_2O \rightleftarrows Na_2SO_4 + 10H_2O$. Similar relationships are, in general, found in the case of other salt hydrates, *e.g.* sodium carbonate hydrates.

Determination of the Transition Point.—For the determination of the transition point of a polymorphous solid or of a salt hydrate, various methods have been employed. The different methods, however, are not equally suitable in

every case ; nor is the value obtained by the different methods always identical. It is well, therefore, to determine the transition point by different methods. The more important of these are : solubility, thermometric, dilatometric, and tensimetric methods.

1. *Solubility Method.*—This has already been studied in the preceding section.

2. *Thermometric Method.*—The thermometric method depends on the fact that change from one system to another on passing through the transition point, is accompanied by a heat effect—absorption or evolution of heat.[1] Thus, when $Na_2SO_4.10H_2O$ breaks up into Na_2SO_4 and solution, heat is absorbed ; while the reverse change is accompanied by evolution of heat.

EXPERIMENT.—*Determine the Transition Point of Glauber's Salt by the Thermometric Method.*

A moderately large quantity (30 to 50 g.) of recrystallized sodium sulphate decahydrate is placed in a thin glass tube, so as entirely to surround the bulb of a thermometer, graduated in tenths of a degree. The tube is placed in a large beaker of water, the temperature of which can be very slowly raised by means of a small flame, and be kept uniform by means of a stirrer. The temperature of the bath is raised to about 32°, at which it may be kept for several minutes, and then very gradually raised until the Glauber's salt becomes partially liquid. The temperature of the bath is then kept constant. The partially liquefied mass in the tube is now well stirred by means of a ring stirrer of glass or platinum, as in carrying out a freezing-point determination with the Beckmann apparatus (p. 126), and the temperature of the mass read off from time to time. Meanwhile the temperature of the bath may be allowed to rise very slowly (1° in 5 minutes), and the temperature of the partially liquefied mass should be read off every minute. After the temperature of the bath and of the partially liquefied mass has risen to about 34°, allow the temperature to fall slowly. Meanwhile stir the sodium sulphate and solution well, and read the temperature every minute.

The temperature readings for the mixture in the tube are plotted against the time, and in this way two curves

[1] This method is not in general suitable for the determination of the transition point of polymorphic forms, on account of the slowness of change and consequent slight evolution of heat in unit of time.

will be obtained, one for rising and the other for falling temperature, each showing an approximately perpendicular portion. Owing to suspended transformation, these two perpendicular portions may not coincide.

Repeat the experiment, but allow the temperature of the bath to rise more slowly between 32° and 33°. Again read the temperature on the thermometer in the tube every minute, and plot the results as before.

Similar determinations may also be carried out with the salts given in Table I. of the Appendix.[1]

3. *Dilatometric Method.*—Since, in the majority of cases, transformation at the transition point is accompanied by an appreciable change of volume, it is only necessary to ascertain the temperature at which this change of volume occurs in order to determine the transition point. For this purpose the *dilatometer* is employed, an apparatus which consists of a bulb with capillary tube attached, and which constitutes a sort of large thermometer (Fig. 119). Some of the substance to be examined is passed into the bulb A through the tube B, which is then sealed off.[2] The rest of the bulb and a small portion of the capillary tube are then filled with some liquid which is without chemical action on the substance under investigation. A liquid, however, may be employed which dissolves the substance slightly.

In using the dilatometer, two methods of procedure may be followed. According to the first method, the dilatometer containing the form stable at lower temperatures is placed in a thermostat, maintained at a constant temperature, until it has taken the temperature of the bath. The height of the meniscus is then read on a millimetre scale attached to the capillary. The temperature of the thermostat is slowly raised, and the height of the meniscus at each degree of temperature noted. If no change takes place in the

FIG. 119.

[1] Richards and collaborators, *Proc. Amer. Acad.*, vols. **34**, **38**, **43**, and **47** ; *Z. physikal. Chem.*, 1898, **26**, 690 ; 1899, **28**, 313 ; 1903, **43**, 465 ; 1908, **61**, 313 ; *J. Amer. Chem. Soc.*, 1914, **36**, 485 ; Hammick, *J. Chem. Soc.*, 1920, **117**, 1589.

[2] Alternatively, the lower end of the bulb may be sealed and the substance introduced through a tubulure on the upper shoulder of the bulb. This tubulure is then tightly closed by means of an accurately fitting ground glass stopper.

solid, the expansion will be practically uniform, or the rise in the level of the meniscus per degree of temperature will be practically the same at the different temperatures, as represented by the line AB in Fig. 120. On passing through the transition point, however, there will be a more or less sudden increase in the rise of the meniscus per degree of temperature (line BC), if the change in the system is accompanied by increase of volume. Thereafter, the expansion will again become uniform (CD). Similarly, on cooling, contraction will at first be uniform, and then at the transition point there will be a relatively large diminution of volume (DE, EF).

If the transformation occurred immediately the transition point was reached, the sudden expansion and contraction would take place at the same temperature. There is, however, always a certain time lag, so that, with rising temperature, the relatively large expansion does not
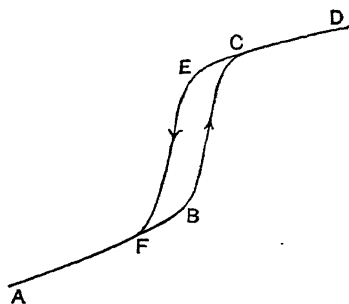
Temperature

FIG. 120.

take place until a temperature somewhat higher than the transition point; and with falling temperature, the contraction occurs at a temperature somewhat below the transition point (*e.g.* BC and EF). The amount of lag will vary from case to case, and will depend on the rapidity with which the temperature is raised and the velocity with which the system changes. After the transition point has been ascertained approximately in this way, the determination is made with greater care, by allowing the temperature in the neighbourhood of the transition point to alter more slowly. In this way the amount of lag is diminished.

Another method of using the dilatometer depends on the fact that while above or below the transition point transformation of one form into the other can take place, at the transition point the two forms undergo no change. The bulb of the dilatometer is charged, therefore, with a mixture of the stable and unstable forms and a suitable measuring liquid, and is then immersed in a bath at constant temperature. After the temperature of the bath has been acquired,

readings of the height of the meniscus are made from time to time to ascertain whether expansion or contraction occurs. If expansion is found, the temperature of the thermostat is altered until a point is reached at which a gradual contraction takes place. The transition point must then lie between these two temperatures ; and by repeating the determinations it will be possible to reduce the difference between the temperatures at which expansion and contraction take place, to, say, 1°, and to fix the temperature of the transition point, therefore, to within half a degree.[1]
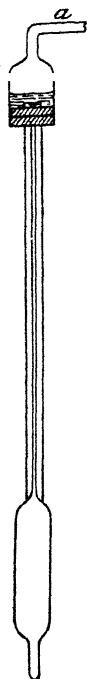
EXPERIMENT.—*Determine the Transition Point for Glauber's Salt and Anhydrous Sodium Sulphate.*

Invert the dilatometer (Fig. 119), and drop into the bulb a small glass bead with stalk, so as to close the end of the capillary tube, and so prevent it being blocked by solid material. Then introduce a quantity of powdered Glauber's salt until the bulb is half or three-quarters full, and seal the end of the tube B. The dilatometer must now be filled with some measuring liquid, *e.g.* petroleum or xylene. This is best done by attaching an adapter to the end of the capillary tube by means of a rubber stopper,[2] as shown in Fig. 121. A quantity of petroleum is introduced into the wider portion of this tube, and the dilatometer then exhausted by means of a water-pump. On now allowing air to enter at *a*, petroleum is driven down into the bulb. The operation is repeated until all the air is withdrawn from the dilatometer and replaced by petroleum. Tap the tube so as to loosen any adhering air-bubbles. The excess of petroleum is then removed from the capillary by means of a long, finely-drawn capillary tube, so that when the dilatometer is placed in the thermostat, the petroleum meniscus may remain on the scale.

FIG. 121.

Immerse the bulb of the dilatometer completely in the water of a thermostat, the initial temperature of which may be 25° to 26°. After about five or ten minutes, read the level of the petroleum, and then slowly raise the temperature, 1° in five to ten minutes, and at each degree again read the

[1] These experiments generally require a considerable period of time.
[2] See also Parker and Lowry, *J. Chem. Soc.*, 1915, 107, 1160.

level of the meniscus in the capillary. At 32° to 33°, it should be found that the rise of the meniscus per degree of temperature is relatively very large; and that as the temperature is raised above 33°, the rise per degree becomes less again and nearly uniform. This shows that the transition point is between 32° and 33°. Carry out the same series of observations in the reverse order, allowing the temperature to fall from about 35° or 36° to about 28°. Then make a more exact determination by allowing the temperature to alter very slowly from 31° to 34°.

EXPERIMENT.—*Determine the Temperature of Formation of Astracanite from the Simple Salts.*

When a mixture of sodium and magnesium sulphates is warmed to 21·6°, partial liquefaction occurs, and astracanite separates out, as represented by the equation—

$$Na_2SO_4.10H_2O + MgSO_4.7H_2O \rightleftarrows Na_2Mg(SO_4)_2.4H_2O + 13H_2O$$
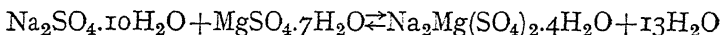
Similarly, on cooling astracanite plus water, formation of $Na_2SO_4.10H_2O$ and $MgSO_4.7H_4O$ occurs on passing 21·6°. This transition point can also be determined by means of the dilatometer.[1]

The experiment is carried out as described under the preceding experiment, the dilatometer being charged with a mixture of Glauber's salt and magnesium sulphate in nearly equimolecular proportions and ground together. The initial temperature of the thermostat may be taken as 15° to 16°.

4. *Tensimetric Method.*—When the systems undergoing change at the transition point possess a measurable vapour pressure, measurements of the latter may be used to determine the transition point. This depends on the fact that at the transition point the vapour pressure of the two systems becomes equal.

For the purpose of these measurements, a differential manometer is employed, the usual form being that known as the Bremer-Frowein tensimeter[2] (Fig. 122). This consists of a ∪-tube, the limbs of which are bent close together, and placed in front of a millimetre scale. The bend of the tube

[1] Van 't Hoff and van Deventer, *Z. physikal. Chem.*, 1887, **1**, 173.
[2] Frowein, *Z. physikal. Chem.*, 1887, **1**, 5; Andreae, *ibid.*, 1891, **7**, 241; Schottky, *ibid.*, 1908, **64**, 415; Menzies, *J. Amer. Chem. Soc.*, 1920, **42**, 1951. An improved form of tensimeter and method of working is described by Hartung, *Trans. Faraday Soc.*, 1920, **15**, Part 3, 150. See also Carpenter and Jette, *J. Amer. Chem. Soc.*, 1923, **45**, 578; Collins and Menzies, *J. Phys. Chem.*, 1936, **40**, 379.

is filled with some suitable liquid, *e.g.* α-bromonaphthalene or olive oil. The substances the vapour pressures of which are to be compared, are placed in the small flasks *d* and *e*, the necks of which are then sealed off. The apparatus is now placed in an inclined position so as to allow the measuring liquid to flow from the bend of the tube into the bulbs *a* and *b*, the tube *f* is connected with a Fleuss or Hyvac pump, and the apparatus exhausted. The tube *f* is then sealed off, and the apparatus, placed in a perpendicular position in a thermostat, is kept at constant temperature until equilibrium is established. The difference of level of the liquid in the two limbs of the tube is read off. In making use of this apparatus, errors are liable to be introduced owing to the slowness with which air is removed from solid phases.
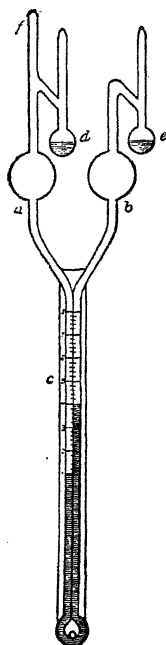
FIG. 122.

EXPERIMENT.—*Determine the Vapour Pressure of Sodium Sulphate Decahydrate (Dissociation Pressure).*

Pure mercury is introduced into the apparatus so as to stand about halfway up each limb of the ∪-tube. In *d* is placed a quantity of Glauber's salt, *finely powdered and mixed with a small quantity of anhydrous sodium sulphate.* Into *e* introduce a quantity of pure sulphuric acid, and seal off both tubes. Incline the apparatus and exhaust by means of a Fleuss or Hyvac pump. Seal off *f*. Immerse the apparatus completely in the water of a thermostat with transparent sides, and regulate the temperature carefully to about 28°. Read the difference in the level of the liquid in the two limbs of the tensimeter after equilibrium has been established. Then raise the temperature degree by degree, and at each point determine the difference of level in the two limbs. Continue the determinations up to 35° or 36°. Represent the results graphically.

EXPERIMENT.—*Determine the Transition Point for Glauber's Salt and Anhydrous Sodium Sulphate.*

At the transition point, the vapour pressure of the crystals $Na_2SO_4.10H_2O$ must become equal to that of the solution saturated for the decahydrate and the anhydrous salt. To test this, the bend of the tensimeter is filled with α-bromo-

naphthalene, and the bulbs d and e are charged respectively with dry powdered crystals of $Na_2SO_4.10H_2O$, and with crystals moistened with a little water, so as to give a saturated solution. The apparatus is exhausted and sealed up as before. It is placed in a thermostat at about $25°$, and the difference of pressure in the two limbs read off when it has become constant. The temperature is then raised degree by degree, and the difference of level of the liquid in the two tubes read off at each temperature.

IV.—FREEZING-POINTS OF BINARY MIXTURES

The investigation of the freezing-points of binary mixtures in which the two components are miscible in all proportions in the liquid state, is of much importance on account of the light which it throws on the conditions under which chemical combination (if any) takes place between the two components. When the two components do not form a stable solid compound, the only systems possible are S_1—L, S_2—L, and S_1—S_2—L, where S_1 and S_2 are the crystalline components and L the liquid solution. (The vapour phase is neglected.) The freezing-point diagram then consists of two curves cutting at a eutectic point.

If, however, one or more stable, solid compounds are formed, the equilibrium diagram will show additional curves representing the composition of solutions with which the solid compounds respectively are in equilibrium.

EXPERIMENT.—*Determine the Freezing-point Curve of Mixtures of Ortho-nitrophenol and Para-toluidine.*

The freezing-points of mixtures of o-nitrophenol and p-toluidine can readily be determined essentially in the same manner as the freezing-points of aqueous solutions (p. 126). A test-tube closed by a cork through which pass a thermometer (graduated in tenths) and a glass rod, the end of which is bent into a loop to serve as a stirrer, is used as the freezing-point tube. It is supported by means of a cork ring in a wider tube which acts as an air-mantle.

After weighing the clean freezing-point tube, a quantity of one of the components is placed at the bottom of the tube, and its weight ascertained. Sufficient of the substance must be taken to ensure that, when molten, it completely covers the bulb of the thermometer. The cork with thermometer is now inserted and the tube, surrounded by its air-mantle

supported in a beaker of water. The temperature of the bath is raised until the substance melts in the freezing-point tube. The bath temperature is then allowed to fall very slowly, and the temperature of the molten substance read off at intervals of half-a-minute or a minute. Stir the molten mass slowly all the time. At a certain point it will be found that crystals begin to separate from the molten mass and the temperature rapidly rises and remains constant. This constant temperature is the freezing-point of the one component. Repeat the determination once or twice.

Now add, from a weighed tube, a quantity of the second component, raise the temperature until all the solid has melted and then allow it to fall slowly and as uniformly as possible. Plot the cooling curve (time against temperature) and note the temperature at which there is a " break " in the cooling curve. Allow the temperature to fall still further until another arrest is shown on the cooling curve and the temperature remains constant until complete solidification takes place. This is the eutectic point. For each composition of the mixture, note the eutectic temperature reached and also the time during which the temperature remains constant at the eutectic point.

Make further additions of the second component, and determine the cooling-curve, freezing-point, and eutectic temperature for each mixture. Mixtures varying in composition by about 10 per cent. of the added component should be made.

Plot the values of the freezing-point (as ordinates) against percentage gram-molecular composition as abscissæ.

With o-nitrophenol and p-toluidine a diagram showing two curves meeting at the eutectic point is obtained.[1] Discuss the meaning of the curves.

EXPERIMENT.—*Determine the Freezing-points of Mixtures of Phenol and Para-toluidine.*

The determinations are carried out in exactly the same way as described above. Discuss the meaning of the curve obtained.[2]

One may also determine the freezing-point curves of naphthalene and p-nitrotoluene ;[3] naphthalene and α-naphthylamine ;[4] phenol and α-naphthylamine.[5] In some

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[1] Philip, *J. Chem. Soc.*, 1903, **83**, 833.
[2] Kremann, *Monatshefte*, 1906, **27**, 91.
[3] *Ibid.*, 1904, **25**, 1246.
[4] Vignon, *Bull. Soc. Chim., France*, 1891 (3), **6**, 387.
[5] Philip, *J. Chem. Soc.*, 1903, **83**, 821.

cases supercooling takes place with great readiness and crystallization of the stable solid phase is very sluggish.

V.—Equilibrium between Liquid and Vapour

Boiling-point Curves of Two Miscible Liquids.[1]—If the external pressure is maintained constant, the boiling-point of a mixture of two completely miscible liquids will vary with the composition. When the curve of total vapour pressure shows neither a maximum nor a minimum, the boiling-point curve will also show neither a maximum nor a minimum ; and the boiling-points of all mixtures will be intermediate between the boiling-points of the pure components. The curve, however, will show a curvature which will be all the greater the more widely the boiling-points of the components are separated. When a solution which gives such a boiling-point curve is distilled, the vapour (distillate) will be richer than the liquid in the component of higher vapour pressure, and the boiling-point will rise as the distillation proceeds. By repeated fractional distillation of such a solution, or by distillation through an efficient still-head, a complete separation of the two components may be effected.

When the vapour pressure curve of the liquid solution passes through a maximum, the boiling-point curve will pass through a minimum ; and when the vapour pressure curve passes through a minimum, the boiling-point curve will pass through a maximum. In such cases, a séparation of the mixture into its pure components cannot be effected by distillation, but only a separation into one or other of the components and a mixture of constant boiling-point (*azeotropic mixture*), the composition of which corresponds to the maximum or minimum point on the boiling-point curve.

Experiment.—*Determine the Equilibrium Liquid-Vapour Curves for Binary Mixtures of Completely Miscible Liquids.*

The boiling-point curves should be determined of one or more of the following binary systems, which are representative of the three classes referred to above :—

1. *Zeotropic Mixtures*, with boiling-points intermediate between those of the pure components :

Benzene (80·2°) : toluene (110·6°).
Benzene : hexane (69·0°).

[1] Young, *Distillation Principles and Processes* (Macmillan).

2. *Azeotropic Mixtures*, with minimum boiling-point :

Iso-propyl alcohol (82·5°) : benzene. Azeotropic mixture (71·9°), 39·3 moles p.c. of alcohol.
Carbon tetrachloride (76·8°) : methyl alcohol (64·7°). Azeotropic mixture (55·7°), 44·5 moles p.c. of CCl$_4$.
Methyl alcohol : benzene. Azeotropic mixture (58·3°), 61·4 moles p.c. of alcohol.

3. *Azeotropic Mixtures*, with maximum boiling-point :

Chloroform (61·2°) : acetone (56·4°). Azeotropic mixture (64·5°), 65·5 moles p.c. of CHCl$_3$.
Water (100°) : formic acid (99·9°). Azeotropic mixture (107·1°), 43·3 moles p.c. of water.

Procedure.—Prepare binary mixtures containing 10, 20, 40, 60, 80, 90 moles per cent. of one of the components, and
determine the refractive index of each mixture at a definite temperature (15° or 20°), using a Pulfrich or Abbe refractometer, and also the refractive index of the pure components. Draw, on a moderately large scale, a graph showing the relation between composition and refractive index.[1]
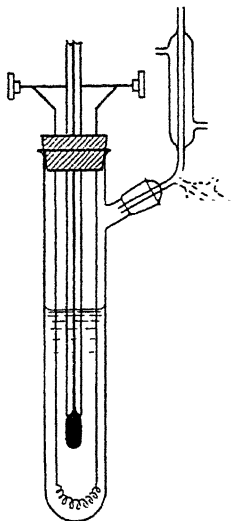
FIG. 123.

First determine the boiling-points of the pure components so that the thermometer readings may be checked and any necessary correction introduced. Then determine the boiling-point of each of the mixtures and the equilibrium composition of the vapour and of the liquid. For this purpose, a quantity of the mixture (70–80 ml.) is placed in a boiling-tube as shown in Fig. 123.   The boiling-tube is fitted, by means of a standard ground glass joint, with a small condenser, and is placed in a Dewar vacuum tube. The apparatus is fitted up so that the liquid can be heated electrically, as described on p. 137. A thermometer, graduated in tenths of a degree, passes through the cork, fitted in the mouth of the boiling-tube, so that the bulb is

[1] In the case of mixtures of water and formic acid, the composition can be determined by titration with sodium hydroxide.

completely immersed in the liquid. The liquid is now caused to boil steadily until vapour is freely forming liquid in the condenser. When vapour is freely condensing and the temperature of the liquid has become constant, the temperature is noted and the condenser is then rotated so that the condensed vapour runs out into a small, cooled weighing bottle. After about 0·5–1 ml. of liquid has been collected (do not collect too much), the heating current is cut off, the cork is removed from the boiling-tube and a small quantity of liquid is removed and run into a small weighing bottle, which is then stoppered and cooled. The refractive index of the distillate and of the liquid in the boiling-tube is determined under the same conditions as before, and the composition of the boiling liquid and of the vapour in equilibrium with it (the distillate) is read from the composition-refractive index curve.

Proceed in the manner described in the case of each binary mixture, and plot the molar percentage composition of liquid and vapour at each boiling temperature in a temperature-composition diagram.

Separation of Mixtures by Distillation.—The vapour in equilibrium with a solution of two volatile liquids is richer than the liquid in the component of higher vapour pressure (lower boiling-point), and, consequently, when the liquid mixture is fractionally distilled, each fraction will be richer in the more volatile component than the liquid from which it is distilled. By subjecting these " fractions " to further fractionation, distillates can be obtained which are progressively richer and richer in the more volatile component, until, in the case of zeotropic mixtures, a complete separation of the components is effected.

When distillation is carried out with a still-head, the necessity of collecting the distillate in fractions is avoided. When distillation is in progress, a temperature gradient is established along the still-head and, on passing upwards, the vapour which condenses is increasingly rich in the more volatile component. In other words, a process of fractional distillation takes place in the still-head, and, under theoretically perfect conditions, the pure component of lower boiling-point drops from the condenser, and the component of higher boiling-point is left in the still.

In the case of liquids which form binary azeotropic mixtures, separation into the two pure components cannot

be effected by distillation, but only into an azeotropic mixture and one or other of the components, depending on the initial composition of the mixture. In the case of liquids which give a boiling-point curve showing a minimum, the azeotropic mixture will be obtained as the distillate, and the residue will be one or other of the components. When the boiling-point curve shows a maximum, the distillate will be one or other of the components, and the azeotropic mixture will be left in the still.

After having obtained the boiling-point curves for a series of binary mixtures, the separation of these mixtures by distillation should be studied, and the efficiency of different still-heads investigated. The constant boiling mixtures, also, should be prepared by distillation, and their composition be thereby more accurately determined.

CHAPTER XVI

COLLOIDS

THE special properties associated with the particular range of subdivision or dispersity to which the term " colloid " is applied, are of such importance, in many different directions, that some familiarity with them is desirable ; and a few experiments, qualitative and quantitative, dealing with some of the electrical and surface properties of colloids are described below.

Dealing only with liquid colloid sols, or systems in which the finely subdivided or dispersed material exists in a liquid *dispersion medium,* we find that two classes are generally distinguished. In the one class, the sols are practically as mobile as the dispersion medium itself, whereas, in the other class, the sols are more or less viscous, *e.g.* solutions of starch or gelatin in water. The sols of the former class resemble, in their behaviour, fine suspensions of solid particles, and are called suspensoid (or lyophobe) colloids ; the sols of the latter class resemble emulsions of oil and water, and are called emulsoid (or lyophile) colloids.

It is mainly with suspensoids we shall deal here.

Electrical Properties of Suspensoids.—Just as the particles of a fine suspension of, say, clay in water are found to be electrically charged, so also are the colloid particles of a suspensoid sol. The existence of such a charge, which is sometimes positive and sometimes negative, can readily be demonstrated by electrophoresis or migration in an electric field. For this purpose one may use a colloidal sol of ferric hydroxide or hydrous ferric oxide (positively charged) or of arsenious sulphide (negatively charged).

Preparation of colloidal ferric hydroxide.—To a half-saturated, freshly prepared solution of ferric chloride add, in drops and with stirring, an approximately 2N-solution of ammonium carbonate, until the precipitate formed just ceases to be dissolved. Filter if necessary and dialyse the liquid in a parchment or cellophane tube against distilled

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water until only a trace of chloride can be detected in the water.

Or, add gradually to 200 ml. of boiling water, 20 ml. of a 2 per cent. solution of ferric chloride. Red-brown ferric hydroxide sol is produced by hydrolysis. When cold, free from hydrochloric acid by dialysis.

Preparation of arsenious sulphide sol.—Boil about 1 g. of arsenious oxide with 500 ml. of water until all is dissolved and allow to cool. (Crystalline arsenious oxide dissolves only very slowly; the amorphous form dissolves more rapidly.) Pass hydrogen sulphide, washed by bubbling through water, into the solution until the latter is saturated. Free the solution from excess of H_2S by means of a stream of hydrogen, and filter.
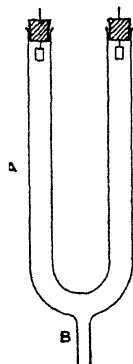
Electrophoresis.—Into the bend of a ∪-tube (A), the limbs of which are about 15 cm. long and 1·5 cm. diameter, is sealed a short length of tubing of about 0·4 cm. bore (Fig. 124). This tube is loosely plugged with cotton-wool, previously well washed, and then connected with a piece of rubber tubing and a funnel. On the rubber tubing, near B, is placed a spring clip. Into the funnel pour a colloidal sol of As_2S_3, so as to fill the rubber tube without air-bubbles. Carefully open the spring clip so as to allow the As_2S_3 sol almost to fill the tube B. Into the ∪-tube pour 6–7 ml. of distilled water, so as to fill the bend of the tube. Lower the reservoir funnel to the level of B, open the spring clip carefully and raise the funnel very slowly. The As_2S_3 sol will in this way be made to rise in the limbs of the ∪-tube, lifting the water with it. When the water has been raised to about 1 cm. from the mouth of the tube, close the spring clip, insert the corks, carrying platinum electrodes, in the ∪-tube, and connect the electrodes with a source of direct current of electricity (100–200 volts). The lower edge of the platinum electrodes should be only 2–3 mm. above the upper surface of the As_2S_3 sol. The whole apparatus should be kept as free from shaking as possible. After a short time, 10–15 minutes, a distinct movement of the yellow sulphide sol towards the anode should be observed.

FIG. 124.

The phenomenon of electrophoresis may also be studied with a suspension of filter-paper fibres (obtained by vigorously shaking

small pieces of filter paper with distilled water). The fibres are negatively charged.

Rubber latex, dialysed so as to remove most of the ammonia used as stabilizer, may also be subjected to electrophoresis, using zinc electrodes. The rubber is deposited on the anode.

With ferric hydroxide sol the movement of the hydroxide should be towards the cathode.

By attaching a millimetre scale to the limb of the U-tube the rate at which the boundary moves can be determined ; and knowing the voltage applied to the electrodes and their distance apart, the rate of movement for a potential gradient of 1 volt per centimetre can be calculated.[1] (Value about 3×10^{-4} cm./sec.)

Precipitation of Suspensoid Colloids.—Colloid particles are, as we have seen, electrically charged, and to this fact, indeed, they owe very largely their stability. When the electric charge on the particles is neutralized, or when two suspensoids of opposite charge are mixed, aggregation of the particles and flocculation or precipitation take place. Suspensoids with charges of the same sign can be mixed without undergoing precipitation.

(a) *Mutual precipitation of Colloids.*—The mutual behaviour of colloids having charges of the same and of opposite sign is demonstrated in an interesting manner by dipping strips of filter paper into the colloidal sols. Filter paper in contact with water becomes negatively charged, and when dipped into the sol of a negatively charged colloid, the latter ascends with the water and spreads through the filter paper. If, however, the colloid is positively charged, it becomes precipitated in the pores of the filter paper after ascending only a short distance.

As positive colloids use a dilute sol of ferric hydroxide or of Night blue (0·2 per cent. sol to which a drop or two of HCl is added) ; as negative colloid use a 0·2 per cent. sol of Alkali blue (to which a drop or two of NaOH is added) or of Congo red.[2]

The mutual precipitation of colloids of opposite charge can best be studied by mixing the sols together. In this case it is found that mutual precipitation takes place only when the colloids are mixed together in certain proportions,

[1] Linder and Picton, *J. Chem. Soc.*, 1897, **71**, 568 ; Whitney and Blake, *J. Amer. Chem. Soc.*, 1904, **26**, 1339 ; Burton, *Phil. Mag.*, 1904 (6), **11**, 425.
[2] Pelet-Jolivet, *Kolloid Zeitscher.*, 1909, **5**, 238 ; Thomas and Garard, *J. Amer. Chem. Soc.*, 1918, **40**, 101.

within rather narrow limits. When excess of one or other colloid is present, precipitation does not occur or does so only incompletely. To show this carry out the following experiment.

Prepare sols of As_2S_3 and of dialysed $Fe(OH)_3$, of 0·5 per cent. concentration (referred to As_2O_3 and Fe_2O_3 respectively). By means of graduated 10 ml. pipettes mix in a series of test-tubes 1 ml. As_2S_3 and 9 ml. $Fe(OH)_3$; 3 ml. As_2S_3 and 7 ml. $Fe(OH)_3$, etc., and determine the relative concentrations at which complete precipitation occurs, and the supernatant liquid remains colourless, after the mixtures have been allowed to stand for one or two hours.

In the above case the optimum amounts will be found to be about 9 ml. As_2S_3 and 1 ml. $Fe(OH)_3$. Vary the proportions by fractions of a millilitre on either side of the optimum point.[1]

(b) *Precipitation of Suspensoid Colloids by Electrolytes.*— Suspensoid colloids are generally very sensitive to electrolytes, so that, in some cases, even quite small quantities of an electrolyte produce precipitation. The " precipitation value " or the concentration of an electrolyte necessary to cause precipitation depends on the nature of the colloid, on the method of its preparation, concentration, etc., as well as on the nature and valency of the electrolyte ions. In the case of positively charged colloids, the precipitation value depends on the valency of the electrolyte anion and is largely, although not entirely, independent of the nature of the cation ; and in the case of negatively charged colloids, it is the valency of the cation that is of primary importance. The higher the valency, the lower is the precipitation value.[2]

The precipitation value of different electrolytes may be studied in the case of As_2S_3 sol or $Fe(OH)_3$ sol.

EXPERIMENT.—*Determine the Precipitation Values of NaCl, CaCl$_2$, and AlCl$_3$ for Arsenious Sulphide Sol.*

Prepare the sol of arsenious sulphide as described on p. 314, using a 0·5 per cent. solution of arsenious oxide. An approximate value of the precipitation concentration may be

[1] Biltz, *Ber.*, 1904, **37**, 1905, 1104.
[2] See Burton and Bishop, *J. Physical Chem.*, 1920, **24**, 701 ; Weiser and Nicholas, *ibid.*, 1921, **25**, 742 ; Kruyt and van der Spek, *Kolloid Zeitschr.*, 1919, **25**, 1.

obtained by running from a burette, into a given volume (say, 50 ml.) of the sol, solutions of known concentration of the different salts.

Having obtained approximate values for the precipitation concentrations, prepare solutions of the salts of appropriate concentration and proceed as indicated below.

1. NaCl.—Prepare a 0·2M-solution of sodium chloride (11·7 g. per litre), and from this prepare a series of 10 ml. portions of diluted solution by mixing, in small test-tubes, 1, 3, 5, 7, 9 ml. of NaCl solution with 9, 7, 5, 3, 1 ml. of distilled water. In five test-tubes of as nearly as possible the same size, and well cleaned by steaming (p. 161), place 10 ml. of the arsenious sulphide sol, and add to each of these in turn one of the five portions of diluted NaCl solution. After each addition, mix well by inverting the tube two or three times, and then place in a rack for a definite time, say, one or two hours. At the end of this time ascertain in which cases precipitation has occurred, and so determine the concentration of NaCl necessary to produce precipitation.

In the above case, 1 ml. of the original NaCl solution contains 0·0002 mole [1] (or 0·2 millimole), and since this amount is then finally diluted to 20 ml., the concentration of the NaCl in the mixed solution will be 10 millimoles per litre ; and in the other cases the concentration will be 30, 50, 70, 90 millimoles per litre. It will be found that in the case of the last two solutions, precipitation has taken place, but not in the case of the first two. In the case of the concentration 50 millimoles per litre, a turbidity will probably be observed. If necessary, further experiments with a concentration of 40 and 60 millimoles can be carried out in order definitely to fix the exact value.

2. CaCl₂.—Proceed in the same way as for NaCl, starting with a 0·005-molar solution of CaCl₂ (0·555 g. per litre). Dilute this in portions as above.

3. AlCl₃.—Prepare a 0·005-molar solution of AlCl₃ (0·668 g. per litre). For stock solution dilute this 10 times, and then dilute in portions as before.

(The precipitation values for the three salts are 51, 0·65, and 0·09 millimoles per litre respectively.)

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[1] Gram-molecule.

Similar experiments can be carried out with other suspensoids, *e.g.* ferric hydroxide sol. In this case, as electrolytes, use NaCl and K_2SO_4. (The precipitation values are 9·25 and 0·20 millimoles per litre respectively.)

Protective Action of Emulsoids.—The precipitating action of electrolytes on suspensoids is diminished by the presence of emulsoid colloids (gelatin, albumin, starch, etc.). Emulsoids are therefore said to exercise a protective action. To illustrate this one may study the concentration of the different emulsoids which will just prevent the precipitation of a suspensoid (*e.g.* As_2S_3) by a certain definite concentration of electrolyte (*e.g.* NaCl). Solutions of gelatin, albumin, and starch are made up, and by systematic dilution (as in the previous experiment), and mixing with a definite volume of As_2S_3 sol, one determines the concentration of emulsoid which just prevents precipitation when 1 ml. of a 10 per cent. NaCl solution is added.

For this purpose one may also use a colloidal gold sol, and take as the indication of precipitation, the change of colour from ruby to blue.[1]   A ruby gold sol suitable for this purpose can be prepared by reduction with formaldehyde or with alcohol, as follows : 5–10 ml. of a 0·01 per cent. solution of gold chloride, neutralized carefully with potassium carbonate (using litmus paper as indicator), are added to 100 ml. of distilled water, and the mixture heated to boiling. To the hot solution, 5–10 ml. of alcohol are gradually added, with shaking, and the liquid then heated for about 20 minutes. The red colour develops slowly, and deepens.   Further small quantities of gold solution and of alcohol can then be added.

Better results are obtained with formaldehyde.   To 100–150 ml. of carefully distilled water are added 1 ml. of a 1 per cent. solution of gold chloride and 3 ml. of 0·2N solution of pure potassium carbonate.   The solution is heated to boiling and then 2–4 ml. of a solution of formaldehyde (obtained by adding 1 ml. of commercial 40 per cent. formalin to 100 ml. of distilled water) are gradually, but fairly rapidly, added.   In a short time the liquid darkens to a pure ruby-red colour.

Adsorption.—The phenomenon of adsorption or increase in the concentration of a substance which takes place in the boundary surface between two phases is one of great importance.   As the amount of adsorption depends on the extent of the boundary surface, the phenomenon can be studied with the help of solid phases possessing a large ·specific surface, *e.g.* porous materials like charcoal or silica

[1] Zsigmondy, *Z. anal. Chem.*, 1902, **40**, 697.

gel, fine powders such as Fuller's earth, or colloids such as ferric hydroxide or aluminium hydroxide.

The phenomenon can be demonstrated by shaking up dilute, but distinctly coloured solutions of iron chloride, methyl violet, Congo red, ferric hydroxide sol with 1–2 g. of animal charcoal. On filtering through filter paper, the colour will be found to have been removed or reduced in strength.

Or, 50 ml. of a 0·1 per cent. solution of quinine sulphate may be shaken with different amounts, 5–10 g., of Fuller's earth or with the special preparation of Fuller's earth known as Lloyd's alkaloid reagent.[1] The filtered liquid is then tested with Mayer's reagent (potassium mercury iodide). As the alkaloid is removed, the precipitate or turbidity obtained diminishes. If sufficient Fuller's earth is used, no precipitate will be obtained on adding Mayer's reagent to the filtrate.

The Adsorption Isotherm.—When charcoal is shaken with a solution of acetic acid, oxalic acid, or other substance which is adsorbed by the charcoal, it is found that the amount adsorbed at a given temperature is given by the expression—

$$\frac{x}{m} = K \cdot c^n$$

where x is the amount of substance adsorbed by m g. of charcoal, c is the concentration of the dissolved substance in the solution at equilibrium, and K and n are constants.

To test this, make up a 0·5N-solution of acetic acid and standardize it against 0·1N-NaOH (using phenolphthalein). Into six conical flasks place (1) 100 ml. 0·5N-acid ; (2) 80 ml. acid + 20 ml. water ; (3) 60 ml. acid + 40 ml. water ; (4) 40 ml. acid + 60 ml. water ; (5) 20 ml. acid + 80 ml. water ; (6) 10 ml. acid + 90 ml. water. To each solution add 2 g. of well-powdered animal charcoal, and shake from time to time during a period of, say, 20 minutes. Filter each solution through a *small* filter paper.[2]

Titrate the filtrate and refer the titrations (ml. 0·1N-NaOH)

[1] Prepared by J. U. Lloyd, Cincinnati, U.S.A. See *J. Amer. Chem. Soc.*, 1913, **35**, 837.

[2] Strictly the solutions should be allowed to stand until the charcoal has completely settled, as the filter paper also adsorbs the acid. If a small filter paper is used, however, the error introduced will be negligible.

to a constant volume (say 10 ml.) of solution. One thus obtains :—

Experiment No. . .	1	2	3	4	5	6
10 ml. of original solution require (in ml. NaOH) .	50·0	40·0	30·9	20·0	10·0	5·0
10 ml. of solution after shaking require (in ml. NaOH) . . .	C_1	C_2	C_3	C_4	C_5	C_6
Amount of acid adsorbed (in ml. NaOH) . . .	$50-C_1$ $=x_1$	$40-C_2$ $=x_2$	$30-C_3$ $=x_3$	$20-C_4$ $=x_4$	$10-C_5$ $=x_5$	$5-C_6$ $=x_6$

If the corresponding values of x/m and c are plotted, a smooth parabolic curve should be obtained. When one takes the logarithms of the quantities in the equation of the adsorption isotherm, one obtains the expression $\log (x/m) = n . \log c + \log K$. That is, $\log (x/m)$ is a linear function of $\log c$, so that if one plots the values of $\log (x/m)$ against the values of $\log c$, a straight line is obtained.

From the results obtained show that the adsorption from dilute solutions is relatively greater than from more concentrated solutions.

Adsorption and Catalysis.—The velocity of many reactions is markedly affected by adsorption. This can be illustrated by the increased velocity of oxidation of oxalic acid when adsorbed on charcoal. The process depends on the kind of charcoal employed, and is also facilitated by the presence of traces of iron.

Connect the following tubes and vessels in series : soda-lime tube, tube with solution of KOH, tube with solution of barium hydroxide, reaction vessel, tube with baryta solution, soda-lime tube. Disconnect the reaction vessel and place in it 5 g. of activated charcoal and 100 ml. of distilled water. Boil the contents for 15 minutes in order to expel CO_2 adsorbed on the charcoal, and then connect the reaction flask in its place. Keep the temperature at 40°–45° by immersion in a water bath. Draw CO_2-free air slowly through the apparatus to free reaction flask from any CO_2. The baryta solution on either side of the reaction

vessel must remain clear. When no more CO_2 is given off from the contents of the reaction flask, quickly introduce 2 grams of oxalic acid into the reaction flask and connect this with a fresh tube of baryta solution. Draw CO_2-free air through the reaction flask, and in 10–15 minutes a distinct turbidity should be seen in the baryta solution.

APPENDIX

INTERNATIONAL ATOMIC WEIGHTS (1940)

		O=16.			O=16.
Aluminium .	Al	26·97	Neodymium	Nd	144·27
Antimony .	Sb	121·76	Neon . . .	Ne	20·183
Argon . .	A	39·944	Nickel . .	Ni	58·69
Arsenic . .	As	74·91	Nitrogen . .	N	14·008
Barium . .	Ba	137·36	Osmium . .	Os	190·2
Beryllium .	Be	9·02	Oxygen . .	O	16·00
Bismuth . .	Bi	209·00	Palladium .	Pd	106·7
Boron . .	B	10·82	Phosphorus .	P	30·98
Bromine . .	Br	79·916	Platinum. .	Pt	195·23
Cadmium .	Cd	112·41	Potassium .	K	39·096
Cæsium . .	Cs	132·91	Praseodymium	Pr	140·92
Calcium . .	Ca	40·08	Radium . .	Ra	226·05
Carbon . .	C	12·01	Rhodium. .	Rh	102·91
Cerium . .	Ce	140·13	Rubidium .	Rb	85·48
Chlorine . .	Cl	35·457	Ruthenium .	Ru	101·7
Chromium .	Cr	52·01	Samarium .	Sa	150·43
Cobalt . .	Co	58·94	Scandium .	Sc	45·10
Copper . .	Cu	63·57	Selenium .	Se	78·96
Fluorine . .	F	19·00	Silicon . .	Si	28·06
Gallium . .	Ga	69·72	Silver . .	Ag	107·88
Germanium .	Ge	72·60	Sodium . .	Na	22·997
Gold . . .	Au	197·2	Strontium .	Sr	87·63
Helium . .	He	4·003	Sulphur . .	S	32·06
Hydrogen .	H	1·008	Tantalum .	Ta	180·85
Indium . .	In	114·76	Tellurium .	Te	127·61
Iodine . .	I	126·92	Thallium .	Tl	204·39
Iridium . .	Ir	193·1	Thorium . .	Th	232·12
Iron . . .	Fe	55·85	Tin . . .	Sn	118·7
Krypton . .	Kr	83·7	Titanium. .	Ti	47·90
Lanthanum .	La	138·92	Tungsten. .	W	183·92
Lead . .	Pb	207·21	Uranium . .	U	238·07
Lithium . .	Li	6·94	Vanadium .	V	50·95
Magnesium .	Mg	24·32	Xenon . .	Xe	131·3
Manganese .	Mn	54·93	Zinc . . .	Zn	65·38
Mercury . .	Hg	200·61	Zirconium .	Zr	91·22
Molybdenum .	Mo	95·95			

TABLE I

TRANSITION POINTS OF SALTS HYDRATES.

	Temperature on hydrogen scale.	Temperature on mercury thermometer.
$Na_2CrO_4, 10H_2O \leftrightarrow Na_2CrO_4, 6H_2O$	19·63°	19·71°
$Na_2CO_3, 10H_2O \leftrightarrow Na_2CO_3, 7H_2O$	32·02°	32·12°
$Na_2SO_4, 10H_2O \leftrightarrow Na_2SO_4$	32·38°	32·48°
$NaBr, 2H_2O \leftrightarrow NaBr$	50·67°	50·78°
$MnCl_2, 4H_2O \leftrightarrow MnCl_2, 2H_2O$	58·09°	58·33°

TABLE II

HEATING LIQUIDS.

	B.-p.		B.-p.
Benzene	80°	Aniline	184°
Water	100°	o-Toluidine	200°
Toluene	110°	Nitrobenzene	209°
Xylene (commercial).	ca. 138°	Naphthalene	218°
m-Xylene	139°	Zuinoline	238°

TABLE III

VISCOSITIES OF LIQUIDS IN MILLIPOISES.

Substance.	0°.	10°.	20°.	30°.	40°.	50°.
Alcohol, methyl . . .	8·08	6·90	5·93	5·15	4·49	3·95
,, ethyl . . .	17·72	14·66	12·00	10·03	8·34	7·02
Benzene	9·00	7·57	6·47	5·61	4·92	4·36
Carbon tetrachloride . .	13·51	11·38	9·75	8·48	7·46	6·62
Chloroform.	6·99	6·25	5·63	5·10	4·64	4·24
Toluene	7·72	6·71	5·90	5·25	4·71	4·26
Water	17·938	13·097	10·087	8·004	6·536	5·492

TABLE IV

Substance.	Surface tension in dynes per centimetre at					
	0°.	10°.	20°.	30°.	40°.	50°.
Water	75·64	74·22	72·75	71·18	69·56	67·91
Ethyl alcohol . . .	24·05	23·14	22·27	21·43	20·60	19·80
Ethyl acetate . .	26·5	—	23·9	—	—	20·2
Carbon tetrachloride .	—	28·00	26·77	25·53	—	23·14
Ethyl ether . . .	—	—	17·01	—	—	13·47
Benzene	31·58	30·22	28·88	27·56	26·26	24·98

TABLE V
IONIC CONDUCTIVITIES AT INFINITE DILUTION.

Kation.	18°.	25°.	Anion.	18°.	25°.
Ag·	54·3	63·5	Br	67·2	77·4
H·	314	350	Cl'	65·5	75·5
K·	64·6	74·5	I'	66·4	76·2
Na·	43·5	50·9	NO_3'	61·7	70·6
NH_4·	64	73·9	OH'	172	192
$\frac{1}{2}Ba$··	55	65	Ac'	35	40·8
$\frac{1}{2}Ca$··	51	60	$\frac{1}{2}C_2O_4''$	63	73
$\frac{1}{2}Pb$··	61·5	72·0	$\frac{1}{2}SO_4''$	68	79
$\frac{1}{2}Mg$··	45	53·1	$\frac{1}{2}CrO_4''$	72	83·6 (?)

TABLE VI
SOLUBILITIES OF SOME SPARINGLY SOLUBLE SALTS.

Salt.	Degree of ionization, per cent.	Solubility (by conductivity) at 20° (grams per litre).
Silver chloride .	100	$1·53 \times 10^{-3}$
,, chromate .	—	$2·7 \times 10^{-2}$
,, bromide .	100	$0·84 \times 10^{-4}$
,, thiocyanate .	100	$1·4 \times 10^{-4}$
Thallous chloride .	90	$3·26 \times 10^{-2}$
Lead chloride .	95·6	$9·61 \times 10^{-1}$
,, iodide .	97	$0·47 \times 10^{-1}$
,, sulphate .	92	$4·3 \times 10^{-2}$

TABLE VII
HYDROGEN ION CONCENTRATIONS AND pH VALUES.

pH (n = a whole number).	Gram-equivalents per litre.	pH (n = a whole number).	Gram-equivalents per litre.
n·00	$1·00 \times 10^{-n}$	n·50	$3·16 \times 10^{-(n+1)}$
n·05	$8·91 \times 10^{-(n+1)}$	n·55	2·82 ,,
n·10	7·94 ,,	n·60	2·51 ,,
n·15	7·08 ,,	n·65	2·24 ,,
n·20	6·31 ,,	n·70	2·00 ,,
n·25	5·63 ,,	n·75	1·78 ,,
n·30	5·02 ,,	n·80	1·59 ,,
n·35	4·47 ,,	n·85	1·41 ,,
n·40	3·98 ,,	n·90	1·26 ,,
n·45	3·55 ,,	n·95	1·12 ,,

TABLE VIII

ACTIVITY COEFFICIENTS OF AQUEOUS HYDROCHLORIC AND SULPHURIC
ACID SOLUTIONS AT 25°.

Molality.	Activity Coefficient (γ).	
	HCl.	H_2SO_4.
0·01	0·924	0·617
0·02	0·894	0·519
0·05	0·860	0·397
0·1	0·814	0·313
0·2	0·783	0·244
0·5	0·762	0·178
1·0	0·823	0·150
2·0	1·032	0·147

TABLE IX

VALUES OF GRAVITY (g).

	g.		g.
Aberdeen	981·7	Greenwich.	981·2
Auckland (N.Z.)	980	Johannesburg.	978·6
Bombay	978·6	Madras	978·3
Boston.	980·4	Melbourne.	980
Brisbane	979·1	Montreal	980·7
Cairo	979·3	Sydney	979·7
Calcutta	978·8	Washington (D.C.)	980·1
Cape Town	979·7	Wellington (N.Z.)	980·3

TABLE X

IONIC PRODUCT OF WATER.

Temperature.	$K_w \times 10^{14}$.	Temperature.	$K_w \times 10^{14}$.
10°	0·295	35°	2·14
15°	0·46	37°	2·45
18°	0·59	40°	3·02
20°	0·69	60°	9·33
25°	1·02	80°	23·4
30°	1·48	100°	51·3

TABLE XI

REDUCTION OF BAROMETRIC READINGS TO 0° C.

When the barometer has a brass scale, the corrected barometric height B_0 is given by the expression,

$$B_0 = B\left[1 - \frac{(\beta - \alpha)t}{(1 + \beta t)}\right]$$

where B and t are the observed height and temperature ; $\alpha = 0\cdot0000184$, the coefficient of linear expansion of brass ; $\beta = 0\cdot0001818$, the coefficient of cubical expansion of mercury.

In the following table are given the corrections in millimetres to be *subtracted* from the observed barometric height.

Temp.	Barometric Readings.			
	720.	740.	760.	780.
10°	1·17	1·21	1·24	1·27
12°	1·41	1·45	1·49	1·53
14°	1·64	1·69	1·73	1·78
16°	1·88	1·93	1·98	2·03
18°	2·11	2·17	2·23	2·29
20°	2·34	2·41	2·47	2·54
22°	2·58	2·65	2·72	2·79
24°	2·81	2·89	2·97	3·05
26°	3·04	3·13	3·21	3·30
28°	3·28	3·37	3·46	3·55
30°	3·51	3·61	3·71	3·80

TABLE XII

REDUCTION OF BAROMETRIC READINGS TO LATITUDE 45° AND SEA-LEVEL.

In the following table are given the corrections (C) in millimetres to reduce the barometric readings, corrected for temperature, to the values at latitude 45°. In latitudes between 0° and 45°, the corrections must be subtracted, and in latitudes between 45° and 90°, they must be added.

Latitude	0° 90°	5° 85°	10° 80°	15° 75°	20° 70°	25° 65°	30° 60°	35° 55°	40° 50°	45° 45°
C	1·97	1·94	1·85	1·70	1·51	1·27	0·98	0·67	0·34	0·00

For each 1000 metres above sea-level, 0·24 mm. must be subtracted from the observed reading.

TEMPERATURE MEASUREMENTS.—CORRECTION FOR EXPOSED STEM.

Since a thermometer is graduated so as to show correct temperatures when the whole of the mercury is immersed in a liquid, a correction must be applied to the observed temperature when a portion of the mercury thread projects above the liquid. If t is the observed temperature, and t' the mean temperature of the emergent thread, the correct temperature, t_0, is given by the expression, $t_0 = 0 \cdot 000143 (t - t') \mathrm{N} + t$. In this expression, N is the length of the exposed stem in degrees. The temperature, t', is ascertained by means of an auxillary thermometer the bulb of which is placed at the middle point of the exposed stem of the main thermometer.

LOGARITHMS.*

	0	1	2	3	4	5	6	7	8	9	1	2	3	4	5	6	7	8	9
10	0000	0043	0086	0128	0170	0212	0253	0294	0334	0374	4	8	12	17	21	25	29	33	37
11	0414	0453	0492	0531	0569	0607	0645	0682	0719	0755	4	8	11	15	19	23	26	30	34
12	0792	0828	0864	0899	0934	0969	1004	1038	1072	1106	3	7	10	14	17	21	24	28	31
13	1139	1173	1206	1239	1271	1303	1335	1367	1399	1430	3	6	10	13	16	19	23	26	29
14	1461	1492	1523	1553	1584	1614	1644	1673	1703	1732	3	6	9	12	15	18	21	24	27
15	1761	1790	1818	1847	1875	1903	1931	1959	1987	2014	3	6	8	11	14	17	20	22	25
16	2041	2068	2095	2122	2148	2175	2201	2227	2253	2279	3	5	8	11	13	16	18	21	24
17	2304	2330	2355	2380	2405	2430	2455	2480	2504	2529	2	5	7	10	12	15	17	20	22
18	2553	2577	2601	2625	2648	2672	2695	2718	2742	2765	2	5	7	9	12	14	16	19	21
19	2788	2810	2833	2856	2878	2900	2923	2945	2967	2989	2	4	7	9	11	13	16	18	20
20	3010	3032	3054	3075	3096	3118	3139	3160	3181	3201	2	4	6	8	11	13	15	17	19
21	3222	3243	3263	3284	3304	3324	3345	3365	3385	3404	2	4	6	8	10	12	14	16	18
22	3424	3444	3464	3483	3502	3522	3541	3560	3579	3598	2	4	6	8	10	12	14	15	17
23	3617	3635	3655	3674	3692	3711	3729	3747	3766	3784	2	4	6	7	9	11	13	15	17
24	3802	3820	3838	3856	3874	3892	3909	3927	3945	3962	2	4	5	7	9	11	12	14	16
25	3979	3997	4014	4031	4048	4065	4082	4099	4116	4133	2	3	5	7	9	10	12	14	15
26	4150	4166	4183	4200	4216	4232	4249	4265	4281	4298	2	3	5	7	8	10	11	13	15
27	4314	4330	4346	4362	4378	4393	4409	4425	4440	4456	2	3	5	6	8	9	11	13	14
28	4472	4487	4502	4518	4533	4548	4564	4579	4594	4609	2	3	5	6	8	9	11	12	14
29	4624	4639	4654	4669	4683	4698	4713	4728	4742	4757	1	3	4	6	7	9	10	12	13
30	4771	4786	4800	4814	4829	4843	4857	4871	4886	4900	1	3	4	6	7	9	10	11	13
31	4914	4928	4942	4955	4969	4983	4997	5011	5024	5038	1	3	4	6	7	8	10	11	12
32	5051	5065	5079	5092	5105	5119	5132	5145	5159	5172	1	3	4	5	7	8	9	11	12
33	5185	5198	5211	5224	5237	5250	5263	5276	5289	5302	1	3	4	5	6	8	9	10	12
34	5315	5328	5340	5353	5366	5378	5391	5403	5416	5428	1	3	4	5	6	8	9	10	11
35	5441	5453	5465	5478	5490	5502	5514	5527	5539	5551	1	2	4	5	6	7	9	10	11
36	5563	5575	5587	5599	5611	5623	5635	5647	5658	5670	1	2	4	5	6	7	8	10	11
37	5682	5694	5705	5717	5729	5740	5752	5763	5775	5786	1	2	3	5	6	7	8	9	10
38	5798	5809	5821	5832	5843	5855	5866	5877	5888	5899	1	2	3	5	6	7	8	9	10
39	5911	5922	5933	5944	5955	5966	5977	5988	5999	6010	1	2	3	4	5	7	8	9	10
40	6021	6031	6042	6053	6064	6075	6085	6096	6107	6117	1	2	3	4	5	6	8	9	10
41	6128	6138	6149	6160	6170	6180	6191	6201	6212	6222	1	2	3	4	5	6	7	8	9
42	6232	6243	6253	6263	6274	6284	6294	6304	6314	6325	1	2	3	4	5	6	7	8	9
43	6335	6345	6355	6365	6375	6385	6395	6405	6415	6425	1	2	3	4	5	6	7	8	9
44	6435	6444	6454	6464	6474	6484	6493	6503	6513	6522	1	2	3	4	5	6	7	8	9
45	6532	6542	6551	6561	6571	6580	6590	6599	6609	6618	1	2	3	4	5	6	7	8	9
46	6628	6637	6646	6656	6665	6675	6684	6693	6702	6712	1	2	3	4	5	6	7	7	8
47	6721	6730	6739	6749	6758	6767	6776	6785	6794	6803	1	2	3	4	5	5	6	7	8
48	6812	6821	6830	6839	6848	6857	6866	6875	6884	6893	1	2	3	4	4	5	6	7	8
49	6902	6911	6920	6928	6937	6946	6955	6964	6972	6981	1	2	3	4	4	5	6	7	8
50	6990	6998	7007	7016	7024	7033	7042	7050	7059	7067	1	2	3	3	4	5	6	7	8
51	7076	7084	7093	7101	7110	7118	7126	7135	7143	7152	1	2	3	3	4	5	6	7	8
52	7160	7168	7177	7185	7193	7202	7210	7218	7226	7235	1	2	2	3	4	5	6	7	7
53	7243	7251	7259	7267	7275	7284	7292	7300	7308	7316	1	2	2	3	4	5	6	6	7
54	7324	7332	7340	7348	7356	7364	7372	7380	7388	7396	1	2	2	3	4	5	6	6	7

	0	1	2	3	4	5	6	7	8	9	1	2	3	4	5	6	7	8	9
55	7404	7412	7419	7427	7435	7443	7451	7459	7466	7474	1	2	2	3	4	5	5	6	7
56	7482	7490	7497	7505	7513	7520	7528	7536	7543	7551	1	2	2	3	4	5	5	6	7
57	7559	7566	7574	7582	7589	7597	7604	7612	7619	7627	1	2	2	3	4	5	5	6	7
58	7634	7642	7649	7657	7664	7672	7679	7686	7694	7701	1	1	2	3	4	4	5	6	7
59	7709	7716	7723	7731	7738	7745	7752	7760	7767	7774	1	1	2	3	4	4	5	6	7
60	7782	7789	7796	7803	7810	7818	7825	7832	7839	7846	1	1	2	3	4	4	5	6	6
61	7853	7860	7868	7875	7882	7889	7896	7903	7910	7917	1	1	2	3	4	4	5	6	6
62	7924	7931	7938	7945	7952	7959	7966	7973	7980	7987	1	1	2	3	3	4	5	6	6
63	7993	8000	8007	8014	8021	8028	8035	8041	8048	8055	1	1	2	3	3	4	5	5	6
64	8062	8069	8075	8082	8089	8096	8102	8109	8116	8122	1	1	2	3	3	4	5	5	6
65	8129	8136	8142	8149	8156	8162	8169	8176	8182	8189	1	1	2	3	3	4	5	5	6
66	8195	8202	8209	8215	8222	8228	8235	8241	8248	8254	1	1	2	3	3	4	5	5	6
67	8261	8267	8274	8280	8287	8293	8299	8306	8312	8319	1	1	2	3	3	4	5	5	6
68	8325	8331	8338	8344	8351	8357	8363	8370	8376	8382	1	1	2	3	3	4	4	5	6
69	8388	8395	8401	8407	8414	8420	8426	8432	8439	8445	1	1	2	2	3	4	4	5	6
70	8451	8457	8463	8470	8476	8482	8488	8494	8500	8506	1	1	2	2	3	4	4	5	6
71	8513	8519	8525	8531	8537	8543	8549	8555	8561	8567	1	1	2	2	3	4	4	5	5
72	8573	8579	8585	8591	8597	8603	8609	8615	8621	8627	1	1	2	2	3	4	4	5	5
73	8633	8639	8645	8651	8657	8663	8669	8675	8681	8686	1	1	2	2	3	4	4	5	5
74	8692	8698	8704	8710	8716	8722	8727	8733	8739	8745	1	1	2	2	3	4	4	5	5
75	8751	8756	8762	8768	8774	8779	8785	8791	8797	8802	1	1	2	2	3	3	4	5	5
76	8808	8814	8820	8825	8831	8837	8842	8848	8854	8859	1	1	2	2	3	3	4	5	5
77	8865	8871	8876	8882	8887	8893	8899	8904	8910	8915	1	1	2	2	3	3	4	4	5
78	8921	8927	8932	8938	8943	8949	8954	8960	8965	8971	1	1	2	2	3	3	4	4	5
79	8976	8982	8987	8993	8998	9004	9009	9015	9020	9025	1	1	2	2	3	3	4	4	5
80	9031	9036	9042	9047	9053	9058	9063	9069	9074	9079	1	1	2	2	3	3	4	4	5
81	9085	9090	9096	9101	9106	9112	9117	9122	9128	9133	1	1	2	2	3	3	4	4	5
82	9138	9143	9149	9154	9159	9165	9170	9175	9180	9186	1	1	2	2	3	3	4	4	5
83	9191	9196	9201	9206	9212	9217	9222	9227	9232	9238	1	1	2	2	3	3	4	4	5
84	9243	9248	9253	9258	9263	9269	9274	9279	9284	9289	1	1	2	2	3	3	4	4	5
85	9294	9299	9304	9309	9315	9320	9325	9330	9335	9340	1	1	2	2	3	3	4	4	5
86	9345	9350	9355	9360	9365	9370	9375	9380	9385	9390	1	1	2	2	3	3	4	4	5
87	9395	9400	9405	9410	9415	9420	9425	9430	9435	9440	0	1	1	2	2	3	3	4	4
88	9445	9450	9455	9460	9465	9469	9474	9479	9484	9489	0	1	1	2	2	3	3	4	4
89	9494	9499	9504	9509	9513	9518	9523	9528	9533	9538	0	1	1	2	2	3	3	4	4
90	9542	9547	9552	9557	9562	9566	9571	9576	9581	9586	0	1	1	2	2	3	3	4	4
91	9590	9595	9600	9605	9609	9614	9619	9624	9628	9633	0	1	1	2	2	3	3	4	4
92	9638	9643	9647	9652	9657	9661	9666	9671	9675	9680	0	1	1	2	2	3	3	4	4
93	9685	9689	9694	9699	9703	9708	9713	9717	9722	9727	0	1	1	2	2	3	3	4	4
94	9731	9736	9741	9745	9750	9754	9759	9763	9768	9773	0	1	1	2	2	3	3	4	4
95	9777	9782	9786	9791	9795	9800	9805	9809	9814	9818	0	1	1	2	2	3	3	4	4
96	9823	9827	9832	9836	9841	9845	9850	9854	9859	9863	0	1	1	2	2	3	3	4	4
97	9868	9872	9877	9881	9886	9890	9894	9899	9903	9908	0	1	1	2	2	3	3	4	4
98	9912	9917	9921	9926	9930	9934	9939	9943	9948	9952	0	1	1	2	2	3	3	4	4
99	9956	9961	9965	9969	9974	9978	9983	9987	9991	9996	0	1	1	2	2	3	3	3	4

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